PRESERVATION AND STORAGE

OF SOUND RECORDINGS

By A. G. PICKETT and M. M. LEMCOE

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A STUDY SUPPORTED BY A GRANT FROM
THE ROCKEFELLER FOUNDATION

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FOREWORD

The phonograph record is a relatively new type of historical document. Although the sound recording as a means of preserving musical performance is its best-known form, music is not the only subject which has gained by the invention of the phonograph. Today there are public and private industrial libraries each of which contains several hundred thousand instantaneous recordings of broadcasts of political and literary significance. These are mostly in the forms of discs and magnetic tapes. Many of these recordings are rare, if not actually unique, and most of them are of great historical importance. There was a time when only large research, university, and industrial libraries collected sound recordings, but now the inclusion of phonograph records in the collections of even small circulating libraries is standard practice. Moreover, the number of private individuals collecting sound recordings and recording equipment has grown enormously, particularly since the advent of the long-playing record and the magnetic tape machine. The phonograph has become very valuable as an aid in the development of the appreciation of music, literature, and other fields of learning.

It is strange that studies on the preservation of sound recordings have previously been neglected, although the problem was becoming more acute with each passing year. The libraries of the country enjoyed the results of basic research for the preservation of paper and motion picture films, but no such information was available for sound recordings. Accordingly, the Library of Congress approached the Rockefeller Foundation for aid in this matter and the Foundation generously made a grant for this purpose. Dr. William Prager, Chairman of the Science Council of Brown University, was the Library's chief consultant in this project and upon his recommendation the experimental work was assigned to the Southwest Research Institute of San Antonio, Texas.

The results of this project are summarized in this report. We believe this to be the first report which attempts to describe existing knowledge on the subject, showing the results of the various tests carried out by the experimentation under the grant, and, equally important, the need for continued work in this field. The report contains information which will be of great use to the Library of Congress in its efforts to preserve its large collection of sound recordings and, we hope, of equal usefulness to the other libraries of this country and other countries as well.

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Librarian of Congress

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ABSTRACT

The purpose of this investigation was to study the storage deterioration of sound recordings in order to establish the optimum storage environments and techniques for library use. This research study was made possible by a grant from the Rockefeller Foundation to the Library of Congress. Playback deterioration (wear) was specifically excluded from this study, which was further limited to phonograph discs and magnetic tape. The significant mechanisms of degradation of each type of recording are discussed and recommendations for storage environments and techniques are presented. The limited experience relating to the aging of plastics and sound records under normal storage conditions preclude accurate estimates of potential shelf life, but the investigation demonstrates that further study would provide means of predicting incipient failure in order to permit re-recording before loss of the records. The life span of a plastic article in an ideal environment is a property which is built into the article when it is manufactured. Proper care cannot extend this potential life although it can prevent premature failure. Presently used sound recording materials are designed for use and economy and not for storage. Because sound records are valuable cultural assets, it is recommended that interested groups should cooperate in the development of sound records of greater potential shelf life than are now available, with particular attention focused on the requirements of the record libraries throughout the country.

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I. INTRODUCTION

Background

The collection, preservation, and dissemination of knowledge are requisite to both the continued operation and the future development of civilization. Within the last few millennia, the medium of memory has been augmented by the more permanent and reliable written or printed record. For many purposes, particularly those of recording history and music, still more accurate recording media have come into use within the last several decades—media which record sight and sound and which, as Mr. John G. Bradley of The National Archives said in 1935 (121), add a second and a third dimension to recorded knowledge. The problem of record storage in terms of space, cost and stability has been considerably increased as libraries have become repositories for motion picture film and sound recordings as well as for books and documents.

Scientific research studies of the storage stability of paper were begun in Europe in the latter part of the 19th century. In this country, a systematic investigation of the problem was undertaken by the Bureau of Standards in the latter part of the 1920's which was given impetus during the 1930's by the National Archives Act and resulted in a rather complete body of knowledge by 1938 concerning the storage and preservation of this kind of record. While much credit must go to the governmental agencies which developed this information within a ten-year period, the contributions made by the paper industry, prior research, and the very existence of paper items which had been stored for very long periods of time must be recognized. The work of the Bureau of Standards on storage degradation of paper has served as a foundation for this and other subsequent studies of the storage degradation of organic materials because of its definition of the parameters of such degradation as well as its development of scientific methods of investigation of this problem.

The study of the problems of storage of motion picture film was initiated in this country by the formation, in 1930, of the Committee on Preservation of Film by the Society of Motion Picture Engineers. The Bureau of Standards, under the joint sponsorship of the National Archives and the Carnegie Corporation of New York, performed a comprehensive research study of these problems under an advisory committee of the National Research Council in 1936 which resulted in the scheme of surveillance of nitrocellulose film by periodic testing for deterioration and the design of storage environment for motion picture film. The experience gained with these techniques together with refinement of procedures by industry and governmental agencies, both here and abroad, within a decade, brought the science of storage of motion picture film abreast with that of book and document storage.

Present Program

In 1954, the Library of Congress, aided by Mr. John S. Coleman of the National Research Council, sought information on the storage of sound recordings comparable to that which had been evolved for paper and motion picture film. While some work had been done by industry and governmental agencies on some aspects of this problem, it was apparent that the complete information required for establishing optimum storage environments and techniques was not available to the librarian. This research study was, accordingly, undertaken by Southwest Research Institute to collect and correlate such information, and to develop suitable techniques for the storage and preservation of disc and magnetic tape sound recordings.

A major part of the effort consisted of the collection and analysis of published information pertaining to the subject, supplemented by laboratory investigations in the fields of mechanics, chemistry and biology. The technical literature of engineering and the basic sciences provided a rich source of valuable information on the behavior and

deterioration of plastics, which was collected and used as a basis for theories of the shelf aging of sound recording materials. Investigations to justify the conclusions arrived at by this synthesis and to explore other avenues in which insufficient knowledge is available included the chemical examination of discs, studies of creep and residual stress in discs, the effects of accelerated and natural shelf aging on discs and tapes, the effects of humidity and fungi on discs, changes in the properties of tapes induced by aging, and storage packaging for sound recordings.

The report is organized in three major sections: "Factors relating to the Degradation of Sound Recording Materials," "The Study of Phonograph Discs," and "The Study of Magnetic Tape." Conclusions and recommendations of specific interest to those responsible for the storage and handling of sound recordings are included individually at the end of each of the latter two sections. In addition, more detailed findings and recommendations with respect to disc recordings are presented at the end of each sub-section of "The Study of Phonograph Discs." Finally, "Recommendations for Future Work" is presented as the last section to indicate the direction of future research necessary if the subject of the storage and preservation of sound recordings is to become a real science. This project was of but a year's duration and must be regarded as a preliminary study in this science; much of the work done has been just sufficient to delineate the problems which must be overcome in order to provide a system of sound recording storage which fits the library requirements of space, availability, cost, and assurance against loss.

While the short history of the use and storage experience with modern sound recording materials is a distinct handicap to the formulation of precise conclusions as to the future behavior of these materials, the results of this study indicate that the potential storage life of existing sound recordings in ordinary library environments is somewhat longer than would be expected by the scientist and considerably shorter than is desirable to the librarian. It should be kept in mind with respect to this problem that resistance to degradation is built into an article at the time of its manufacture by material formulation and processing technique. Most sound recording media were not designed for long-time storage but for playback qualities and low-cost manufacture. Continuation of this work should produce two desirable results: (1) more knowledge

about existing sound recording media, and (2) the development of sound records better suited to library storage than those presently available.

Three systems of recording sound are used; these are groove patterns, magnetic patterns, and photographic patterns. Many variants of these systems have been used, but the bulk of library sound record collections consists of phonograph discs, magnetic tapes and motion picture sound track. This study is restricted to phonograph discs and magnetic tapes, and, even more specifically, to those kinds of discs and tapes which have been produced in great quantity in the United States. The kinds of sound records studied were:

    (1) Phonograph discs
        (a) Acetate (cellulose nitrate)
        (b) Shellac and shellac type
        (c) Vinyl
    (2) Magnetic tapes
        (a) Cellulose acetate base
        (b) Mylar base

Some important categories have been, of necessity, neglected. These categories include styrene discs and polyvinyl chloride base tapes which are certain to form part of any large collection as well as less common items such as wax discs, wire, paper base tape, and cylinder records. In addition, only shelf aging was considered although the interaction of playback and storage is, undoubtedly, of significance in the aging process. Even with these limitations, it was necessary to curtail the amount of work on each type of sound record studied. Most regrettably, it was not possible to make a comprehensive survey of library environments and sound recordings in storage in order to assess the effects of storage in different basic environments; this type of work was confined to the Library of Congress, in Washington, D.C., where the basic environment is superior to many areas with respect to atmospheric contaminants and temperature extremes and is inferior to many areas with respect to humidity conditions. Washington, D.C., has a climate classified as humid subtropical (92) which permits stack temperature control to be maintained as shown in Figure 1 by heating and ventilation alone and has little industry to provide air contamination. Humidity is a serious problem in Washington, D.C., as is indicated in Table 1 (also see Table 1.9 and Fig. 1.13 of Ref. 92). Variations in climatic conditions are bound to cause variations in shelf aging characteristics in different localities, and it is unfortunate that this parameter could not be examined more thoroughly.

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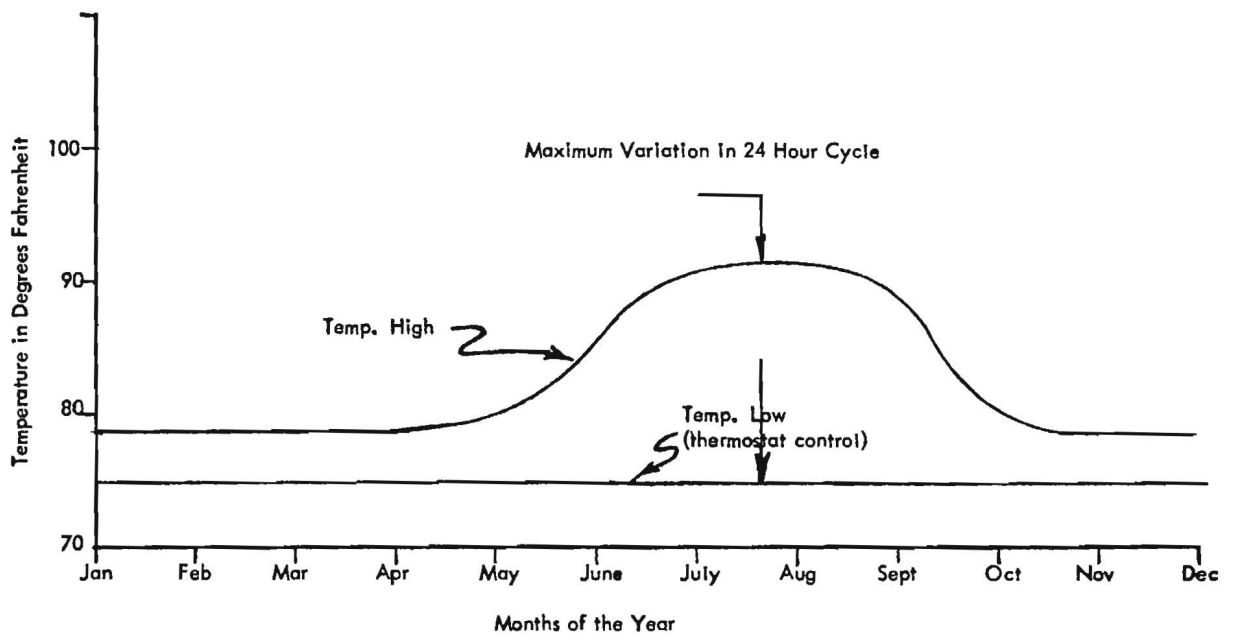
Figure 1. Temperature in a stack provided with heating and air circulation only.
(Northeast Bookstacks, Library of Congress, 1957)

Table 1.—WASHINGTON, D.C., HUMIDITY

Relative Humidity (Percent)

	1:30 A.M.			7:30 A.M.			1:30 P.M.			7:30 P.M.		
	Av.	High	Low	Av.	High	Low	Av.	High	Low	Av.	High	Low
JANUARY	70	100	27	74	100	25	58	100	20	64	100	16
FEBRUARY	67	100	34	72	100	28	54	98	17	60	100	20
MARCH	66	100	32	72	100	20	50	100	17	58	100	9
APRIL	68	100	27	68	100	20	46	98	17	55	100	14
MAY	77	97	37	72	100	26	48	95	12	62	100	18
JUNE	82	99	35	75	100	28	53	100	23	67	100	23
JULY	84	98	37	79	99	41	54	97	26	68	100	29
AUGUST	85	98	54	80	100	41	55	99	25	72	100	19
SEPTEMBER	84	99	46	81	100	44	55	100	26	74	100	22
OCTOBER	81	100	33	80	100	36	52	100	23	70	100	19
NOVEMBER	73	100	35	76	100	24	53	96	12	64	100	21
DECEMBER	73	100	30	75	100	25	59	100	17	65	100	18
YEAR	76	100	27	75	100	20	53	100	12	65	100	9

NOTE.—Information taken from *Climatic Handbook for Washington, D.C.*, Weather Bureau Technical Paper No. 8. Readings are averages of readings for 31 years through 1945.

II. FACTORS RELATING TO THE DEGRADATION OF SOUND RECORDING MATERIALS

A. Manufacture

It was mentioned in the introduction that the resistance of an article to degradation is built into the article at the time of its manufacture. The potential storage life of plastics, the basic materials used for the manufacture of most sound recordings, is particularly dependent upon this parameter. Unfortunately, the effects of this parameter are not, at present, subject to quantitative evaluation. The uncontrolled variables are the basic resin, the materials added to the basic resin to alter its properties to those desired, and the sound record manufacturing process. The quality control of the individual chemical plant producing a basic resin may be excellent and result in a uniform product, but there are numerous sources of these resins including some foreign sources which have sold some extremely low-cost resins on the domestic market. Since chemical degradation can be initiated by but trace amounts of certain chemicals, it would be remarkable if the process differences between chemical plants did not cause differences in resistance to degradation.

The materials added to the basic resin are even more variable in nature than is the resin. The major sound record manufacturers differ significantly in their formulations for cost or product improvement reasons. An unfortunate choice of lubricant or extender can conceivably decrease the potential life of a stored plastic by several decades while a change in stabilizer (see page 23) might increase such life by as much as a century without any noticeable change in appearance or playback quality of a new recording.

The conditions of heat and stress imposed on a plastic during the manufacturing processes are severe. The variation in processing techniques, even if these variations are but ostensibly minor differences in cycle time, temperature or pressure, contribute greatly to variations in such parameters as internal stress, laminate adhesion, retained solvent and chemical degradation initiation. All of these items which make for a variation in potential storage life of sound recordings are outside of the ken and the control of those who acquire and store sound recordings. The only way to overcome this deficiency is to develop suitable specifications covering formulation and manufacture to be used for the procurement of sound recordings which will provide a product of dependable and maximum storage life. Premium sound recordings manufactured under such specifications would undoubtedly be more costly than regular items, but the overall economy which would result from reduced care and longer time intervals between re-recording necessitated by record deterioration would—by far—more than offset this initial expense. From the inquiries received during this program, it seems likely that there is sufficient demand for premium life sound recordings to justify their manufacture.

B. Handling and Storage

One important factor responsible for the reduction of potential storage life can be eliminated without further research. This factor is the environmental history of the sound record between manufacture and acquisition. Quality sound recordings or recording materials are kept in good environment until they are packaged and, usually, after they are received in a library for use and storage. In the interim of warehousing and transportation, however, they are often subjected to severe environments which may materially reduce their potential shelf life. Plastics, because of their degradation mechanisms, are particularly susceptible to damage induced by such treatment. The chemical and physical reactions which cause failure are not evidenced by noticeable changes in appearance or quality during an induction period (a period during which internal chemical reactions occur that initiate the actual degradative reactions)

which often precedes rapid degradation or during the early stages of degradation. These reactions are accelerated by elevations of temperature and, sometimes, by moisture and cyclic changes in temperature or moisture content. The moisture problem can be solved by proper packaging prior to warehousing or transportation, but the temperature problem is far more difficult. It can be solved, however, by obtaining supplies which have not been stored in adverse environments and by proper choice of a carrier to obviate exposure to either extremes of high or low temperature. In some instances this might require shipment in an air-conditioned truck. Libraries, of course, do not have control over many items they receive, but they can, undoubtedly, benefit by controlled procurement of many items.

The storage conditions are controllable by the librarian to an extent permitted by allotted space and funds as well as the requirement of ready availability of the sound records. Optimizing these conditions will not prevent degradation but can definitely inhibit it. The storage conditions are mainly determined by the parameters of physical, chemical and biological degradation of the basic plastic constituents generally used in the manufacture of sound recordings.

C. Properties of Plastics

A plastic is a high-molecular-weight organic compound which is capable of being formed into a desired shape by application of heat, pressure, evaporation of a solvent, solution of a dispersed resin in a plasticizer, or a combination of these techniques. For reasons of economy, as well as to provide more desirable properties, other substances such as plasticizers, softeners, lubricants, extenders, fillers, stabilizers, and pigments, are generally incorporated into a plastic. At the present time, sound recordings are generally made of synthetic or partially synthetic thermoplastics. Thermoplastics are materials that will repeatedly soften when heated and harden when cooled. There is no abrupt change, at the service temperatures of these materials, between the fluid and solid states, but, instead, a thermoplastic gradually becomes softer as the temperature increases.

Plastics *per se* are no more susceptible to degradation than are other materials. They have been manufactured and used for such a short time, however, that the experience with and consequent

knowledge of their long-time behavior is very limited. This deficiency in knowledge is aggravated by the fact that the manner of degradation of plastics is often quite different from that of other more familiar materials such as paper or leather. While polyethylene is not used in the manufacture of sound recordings, the history of this material provides a good example of this characteristic of plastics. Polyethylene is a synthetic hydrocarbon chemically similar to naturally occurring paraffin wax, but with a higher molecular weight. The first users of polyethylene, who were quite familiar with the stability of paraffin waxes, assumed that polyethylene would have the same inherent resistance to deterioration. They were correct in this assumption, with an exception that caused many unforeseen failures. Actually, polyethylene is extremely susceptible to photo-oxidation because of very minute imperfections in its chemical constitution which are not present in natural hydrocarbon waxes. This deficiency has been overcome by the incorporation of anti-oxidants and light-absorbing pigments into the plastic, which increases the outdoor life of polyethylene as much as thirty-fold. This points up another important feature of plastics. That is, the properties of plastics can be altered remarkably by additives in order to achieve a desired result. In general, more than one of the properties of a plastic are changed when an additive is used. In this case, the use of a light-absorbing pigment also changes the color of the polyethylene, which may or may not be desirable. Often, other less obvious and more undesirable property changes are caused in this manner. For example, one could easily choose a heavy-metal soap for incorporation in a plastic as a lubricant which would unforeseeably catalyze the oxidation of the plasticizer used and materially reduce the useful life of the plastic. Because of the interaction between all of the different constituents of a plastic-based article, the deteriorative characteristics of such an article are not determined by those of the basic plastic alone, and due regard must be given to each constituent and its effect on the useful life of the article.

The basic thermoplastic, or resin, is composed of long chain molecules, and its physical properties are dependent on the size and shape of the molecules and the forces between the molecules. The properties of such a resin can be changed chemically by:

(1) Chain scission, which reduces the molecular size.

(2) Cross linking, which changes the type of forces between molecules.

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(3) Side group modification, which changes the amount of the forces between molecules.

D. Atmospheric Factors

The physical properties of a resin can also be altered by changes in temperature, stress, or moisture content. Chemical and physical changes are usually not independent, many different changes taking place simultaneously. A sufficiently large change in the physical properties of a plastic obviously results in failure of the plastic of which the article is made. The manifestation of this failure, in sound recording materials, may be permanent deformation, embrittlement, cracking, loss of adhesion between laminates, or loss of strength. There are two kinds of chemical changes in plastics: internal reaction and reaction with environmental agents. The most important changes are those reactions with the environment or environmentally induced internal reactions.

Radiant energy, in particular the ultraviolet or high frequency portion of the spectrum, should be denied access to sound recording materials, since it is an extremely effective agent of degradation initiation. They should not be exposed to natural sunlight or artificial ultraviolet.

Thermal energy is responsible for both physical and chemical changes in plastics. The physical changes, including changes in size and shape, result mainly from the high coefficient of thermal expansion together with the low thermal conductivity found in most plastics and the changes in viscosity induced by changes in temperature. Permanent deformation or delamination may result from either exposure to an extreme of temperature or cyclic changes in temperature. Chemical changes are accelerated by elevation of temperature. At service temperatures and for most reactions (especially those where water is involved), the reaction rate is approximately doubled for an increase in temperature of 15° F. It would seem that the optimum storage temperature for a material would be as cold as is attainable. This is true to a degree. It must be remembered that temperature changes are harmful, especially abrupt ones, and that the physical properties of plastics are radically changed by extreme changes in temperature. For this reason, it is best to choose a storage temperature (i.e., 60° F to 70° F) which is a compromise between human comfort and the desired reduction of thermal energy to maintain essentially the same temperature in both storage and playback. Sharp temperature changes may thus be avoided. For precious and seldom-used records, it is feasible (and practiced by at least one sound record manufacturer in master tape storage) to store recordings at 15° to 20° F below such a temperature. Much lower temperatures than this create new problems—such as extreme brittleness, ice crystal formation, and failure due to the differing coefficients of expansion of constituent materials.

Moisture is also both a physical and a chemical agent of degradation. Changes in moisture content can cause large dimensional changes in some resins and fillers, which may induce failure, and can also change important physical properties such as impact strength. As a chemical agent, water can either react directly with a resin (hydrolysis), can catalyze other reactions, or can act as a solvent. The solvent action of water is most important both because it enables some compounds to be transported from one place to another in a material and because it enables reactions to take place which only occur in solution. Excess moisture will also provide an environment conducive to biological deterioration.

For the range of materials involved in sound recordings, the optimum moisture content must be less than that which is high enough to promote significant chemical or biological deterioration and at the same time greater than that below which the desired physical properties of some plastics are impaired. For those materials such as the cellulosics, which absorb large amounts of water and undergo large dimensional changes thereby, it is desirable to keep the environmental humidity as constant as is feasible. For service temperatures, the desirable humidity is between 45% R.H. and 65% R.H.

Moisture is present in three forms in a storage environment: water vapor, water films, and combined water. These three forms exist in equilibrium with each other in a closed system. That is, the thickness of a water film on an article, and, sometimes, the amount of combined water, is dependent upon the ambient temperature and the amount of water vapor in the environmental atmosphere; in short, the relative humidity.

Oxygen can be a serious or a minor cause of chemical degradation in plastics. The seriousness of oxidative degradation is, in general, dependent upon the nature of the plastic and the environmental parameters. If a resin molecule is perfectly constructed according to its textbook formula

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and oxidative catalysts are absent, the resin would be unaffected by ordinary oxygen. Reaction sites for oxygen are, however, provided by deviations from the ideal chemical structure of the resin from the moment of manufacture. Light, heat, and chemical changes of the resin which occur during processing and aging provide further reaction sites for oxidative degradation. In general, a well made plastic of good materials is little affected by oxidation if kept in a storage environment free from light and excessive temperature. A few exceptions have been noticed in the past—in particular, the use of raw castor oil as a plasticizer and the effects of molding temperatures on vinyls in the absence of sufficient stabilizing additives have caused trouble—but all presently made materials seem to be quite stable in the presence of oxygen and in the absence of light, excessive temperature, certain trace impurities, and excessive moisture. Ozone is a different problem. In general, however, it will not be a problem in library storage especially if the sound recordings are packaged in materials which will deny access of ozone to the plastic.

Atmospheric contaminants can cause chemical degradation of plastics. These contaminants are principally the oxides of carbon, sulfur, and nitrogen. These contaminants require moisture and free air circulation to be of significance. That at least one of these contaminants can be a serious source of degradation in library environments has been demonstrated in the case of sulfur dioxide and leather book bindings. (94) Properly packaged materials of proper moisture content will not be affected even in heavily contaminated environments and so this need not be a source of degradation if sound recordings are properly protected.

Dust and grit are sources of both physical and chemical degradation of sound recording materials. Physical damage can be caused by scratching of the surface or embedment of dust particles in the surface—either of which affects playback qualities. The surface of an acetate disc may be scratched by the mere withdrawal of it from a paper envelope. Dust is also not an inert material but can provide acid radicals as well as metallic ions which sometimes catalyze degradative processes (see Table 2, which contains data from Washington, D.C., a non-industrial city). Dust films attract moisture and, just as for the gaseous atmospheric contaminants, moisture is essential to their chemical action on materials.

Unfortunately, the thermoplastic is a poor conductor and is electrostatically charged from the molding process with a volume charge* which maintains a surface charge for a long period of time. (120) The surface charge, which is renewed during handling and playback, attracts dust to the surfaces of thermoplastics and holds it there.

The first precaution, of course, to prevent damage by dust is to provide as dust free an environment as is feasible. The sound recording materials should be properly packaged during storage and use facilities should be kept as dust free as possible. The next step is to keep the moisture content of the environment low enough to prevent chemical action of reactive dust constituents. These steps will reduce the dust problem but will not eliminate it. This means that sound recording materials must be cleaned without damaging them.

The major types of chemical degradation of the basic resins have been noted as changes in physical properties resulting from:

(1) Chain scission.
(2) Cross linking.
(3) Side group modification.

induced by:

(1) Light.
(2) Heat.
(3) Water.
(4) Oxygen.
(5) Atmospheric contaminants.
(6) Dust and grit.

The major types of physical degradation of the articles made from these basic resins have been noted as:

(1) Permanent deformation.
(2) Breaking, tearing, or delamination.

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*Electrostatic charges are presumed to result from a temporary excess of or deficiency of electrons in a solid body. In non-conducting materials this is usually restricted to the atoms on the surface of the body, and such a charge is readily dissipated by discharge to ground. Many plastics, however, develop such charges within the volume of the material during molding. These charges are not readily dissipated because of the limited electron mobility of the non-conducting material and serve as an electrostatic charge "reservoir". These charges can induce a surface charge without themselves being dissipated (in the same manner that a charged rod can be used to charge an electroscope without dissipation of the rod charge) or can gradually "leak" to the surface. Volume charges in vinyl discs are of random sign and intensity, and induce correspondingly random surface charges. A surface charge caused by wiping a disc with a particular material will have a sign and intensity determined by the material rubbed against the plastic.

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TABLE 2.—INORGANIC ANALYTICAL DATA, WASHINGTON, D.C., CARDOZO HIGH SCHOOL (B)

From Dust Samples µg/Cu M

Sampling Date	Sam. No.	Particulate	Mn	Pb	Sn	Fe	Cu	Ti	V	Zn	Cr	Ni	Mo	Co	Bi	Cd	Sb	Ba	Be	Cl-	SO4-	NO3-	pH
2/23-24/55	2982	198	0.02	0.6	0.01	0.8	0.05	0.03	0.06	0.4	0.003	0.02	Trace	<0.004	0.002	0.002	<0.1	<0.007	<0.002	0.1	22.7	0.9	5.7
4/28-29/55	2991	146	0.02	0.8	0.004	0.7	0.04	0.02	0.07	0.5	0.002	0.02	Trace	<0.003	<0.002	0.002	<0.1	0.02	Trace	0.1	14.0	0.9	5.7
5/4-5/55	2992	390	<0.01	0.5	<0.004	0.2	0.04	0.01	0.08	0.2	<0.002	0.02	<0.007	<0.004	<0.002	<0.002	<0.1	<0.007	<0.002	0.1	17.6	0.9	5.6
5/12-13/55	2993	165	0.02	0.9	0.02	0.9	0.03	0.02	0.08	0.4	0.002	0.03	<0.007	<0.004	0.002	0.003	<0.1	0.02	Trace	0.1	19.0	1.4	6.6
5/16-17/55	2994	201	0.04	0.9	0.008	1.1	0.02	0.07	0.08	0.4	0.009	0.02	Trace	<0.004	<0.002	0.002	<0.1	0.02	<0.002	0.1	22.6	0.6	5.8
6/6-7/55	2997	133	0.05	0.8	0.03	1.3	0.06	0.02	0.08	0.7	0.01	0.04	Trace	<0.003	0.002	0.004	<0.1	0.04	Trace	0.1	14.8	0.8	5.5
6/27-28/55	3000	125	0.03	1.2	0.006	0.8	0.02	0.02	0.03	0.3	0.006	0.01	<0.007	<0.004	0.002	0.002	<0.1	0.03	Trace	0.1	20.6	0.4	5.6
7/5-6/55	5226	184	0.03	1.0	0.01	1.3	0.02	0.02	0.09	0.4	0.002	0.03	Trace	<0.004	0.002	0.003	<0.1	0.02	<0.002	0.1	26.1	0.7	5.1
8/1-2/55	5231	100	0.02	0.7	<0.003	0.7	0.02	0.01	0.03	0.2	0.003	0.01	<0.007	<0.004	<0.002	0.002	<0.1	0.02	Trace	0.1	12.5	0.1	5.5
8/10-11/55	5232	70	<0.01	0.5	<0.003	0.3	<0.01	0.008	0.03	0.4	<0.002	0.008	<0.006	<0.004	<0.002	0.002	<0.1	0.02	<0.002	0.1	11.9	0.4	5.7
8/29-30/55	5234	168	0.02	0.7	0.01	0.6	0.02	0.02	0.09	0.5	0.003	0.02	Trace	<0.004	0.002	0.002	<0.1	0.006	<0.002	0.1	24.5	1.0	4.4
9/12-13/55	5236	141	0.06	1.4	<0.003	1.0	0.01	0.02	0.05	0.3	0.002	0.02	Trace	<0.004	<0.002	0.002	<0.1	0.01	<0.002	0.2	14.6	0.9	6.3
9/26-27/55	5238	139	0.05	1.9	0.006	1.9	0.02	0.03	0.08	1.4	0.004	0.03	Trace	<0.004	0.002	0.005	<0.1	0.007	<0.002	0.1	17.9	2.1	5.7
10/3-4/55	5239	246	0.03	2.5	0.006	1.5	0.02	0.03	0.1	0.5	0.006	0.04	Trace	<0.004	0.002	0.002	<0.1	0.02	<0.002	0.2	27.4	0.9	4.9
11/28-29/55	5247	177	<0.02	0.6	<0.004	0.4	0.02	0.03	0.1	0.1	0.002	0.02	Trace	<0.004	0.002	<0.002	<0.1	<0.008	<0.002	0.1	18.3	0.7	6.2
1/24-25/56	7281	218	0.06	1.4	<0.004	2.0	0.03	0.05	0.2	0.4	0.008	0.04	Trace	<0.004	0.002	<0.002	<0.1	0.01	Trace	0.1	24.1	1.8	6.0
2/28-29/56	7286	158	0.06	1.0	<0.004	1.2	0.03	0.03	0.1	0.6	0.008	0.03	Trace	<0.005	<0.002	0.003	<0.2	<0.008	<0.002	0.2	25.2	1.1	6.8

(3) Scratching or particle embedment.

induced directly or through temporary changes in physical properties by:

 (1) Temperature changes or excessive temperature.

 (2) Moisture content changes or extremes of moisture content.

 (3) Dust and grit abrasion or embedment caused by removal of record from jacket, horizontal stacking, or playback.

 (4) Stress.

E. Compounding and Additives

Degradation may also be induced by deterioration of other constituents of a plastic than the basic resin, and by the action of the deterioration products of other constituents on the basic resin. The main sources of trouble from these causes are plasticizers, fillers, and extenders.

The physical properties of a basic resin are often not exactly those desired. Cellulose nitrate, for example, is too tough and brittle for use as a coating for instantaneous recordings. These properties may be changed by plasticization. A plastic may be internally plasticized by the copolymerization of a foreign monomer into the basic chain molecule or by a polymer blending. The copolymers or polyblends are usually as stable as the basic resins. Plastics may be externally plasticized by a solvent plasticizer or a softener. The difference between these two types of external plasticizer might be compared to the difference between a solution and a mixture. Loss of an external plasticizer means a loss of the desirable property for which it was introduced and, often, a loss in volume of the plastic. Usually, a solvent plasticized system is more stable than a softener plasticized system. Camphor plasticized cellulose nitrate, for example, is a more stable plastic than castor oil plasticized cellulose nitrate. This is because camphor forms a complex with the cellulose nitrate while castor oil is not chemically combined with the cellulose nitrate. An external plasticizer may be lost by volatilization, extraction, exudation, wicking, chemical degradation or biological consumption. External plasticizers are not only lost by chemical degradation, the products of their deterioration may induce chemical degradation of the basic resin.

Fillers may be used to modify the physical properties of a resin (as in shellac) or for economy (as in some vinyl discs). The more common fillers are limestone, clay, cellulosic by-product flours, plant fibres, and carbon black. These fillers are protected from attack by the environment by their resin coating, but can be attacked by anything which diffuses through the resin. Carbon black is not only inert but protects the basic resin against the action of light by absorbing radiant energy. Limestone is attacked only in the presence of water. Clay is affected only by changes in moisture content (a swelling and shrinking response to such changes). The cellulosic by-product flours and plant fibers swell and shrink with moisture changes and, in the presence of moisture, are chemically attacked by the same agents as are the basic resins and by the decomposition products of both resin and plasticizer. Because of the wide range of kinds and amounts of fillers used, no general statement about their contribution to the potential longevity of a plastic can be made. Fortunately, the same storage environment which inhibits deterioration of the basic resins also inhibits the deterioration of fillers. Moisture content control is the most important feature of a storage environment as far as fillers are concerned.

An extender is an organic material blended with the basic resin usually for the purpose of economy. Natural waxes and resins obtained by the destructive distillation of wood or plant fibres are usually used. In general, they are less stable than the basic resin and reduce the potential storage life of the plastic. Again, they are attacked by the same degradative agents as other organic materials and their deterioration is inhibited by the same environmental control as should be provided for the basic resin.

One other possible constituent of plastics which decreases its potential storage life is residual solvent. When a plastic article is fabricated by evaporation of a solvent, some of the solvent is entrapped by the resin. Because the manufacturer wishes the article to be immediately usable, the plastic formulation is usually designed so as to provide the proper physical properties with this amount of residual solvent. Over a period of time, this residual solvent may gradually diffuse from the plastic and change its properties just as does loss of plasticizer. It is, in fact, difficult to draw a hard and fast line between a solvent and a plasticizer as far as action goes, but process solvents must be much more volatile than are solvent plasticizers, and, hence, are lost by volatilization in a shorter period of time.

There is one characteristic of sound recording materials which affects their degradation which

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should not be forgotten. Sound recording media are designed primarily for fidelity of reproduction of sound and playback durability. Almost without exception, the design of a new material or type of sound recordings has been based on these considerations and economy of manufacture alone. In use, these materials reveal their deficiencies, including those which cause early failure in extended storage. As these deficiencies are recognized, the product is improved to provide longer lasting sound recordings. As a result, it is very difficult to predict the behavior of today's sound recordings from those of yesterday, except to guess that they will be better and longer lasting. Most of these materials are still in the development stage and a collection covering but a few years span will include items superficially identical but of vastly different potential longevity.

F. Fungal Action

An important cause of degradation can be fungal action. The fungi play an indispensable role in the carbon cycle on which life is based by converting the waste products of life into usable compounds and thereby keeping the building blocks of organic materials in circulation. In order to do this efficiently, they have evolved into a very large and heterogeneous group of organisms which attack a tremendous range of organic materials and have an equally wide range of acceptable environments for growth and reproduction. Two of their methods of propagation, by air borne spores and mycelial fragments, are so efficient that the exposed surface of any material in ordinary environments is continually being inoculated by a changing variety of these organisms. Whenever the correct combination of proper organic material, environment, and organism occurs, growth of the fungus and degradation of the material results.

It is not surprising to find that fungi are a significant cause of deterioration of the organic ingredients used in sound recording materials. There are, however, a number of features of fungal activity which are surprising to the non-mycologist. Not the least of these are some of the manifestations of fungal degradation. For example, one quickly connects decay of bread with the garden of mold on its surface, but is not liable to suspect that the stiffening of his raincoat arises from plasticizer consumption by an invisible horde of allied organisms. Another surprising feature of fungal action is the variety and kind of chemicals they manu-

facture. The fungi must digest their food outside of their cellular structure and so excrete both enzymes and acids which attack not only the nutrient media but other materials. A striking example of this is the etching of glass by fungi whose nutrient is an oily fingerprint on the glass. During the storage life of a sound record, it may be exposed to the proper conditions and seriously damaged by fungi. Inspection of the record at a later date may reveal the damage but not the cause since many of the manifestations of fungal activity duplicate degradation by other agents. This makes a study of the causes of deterioration of naturally degraded sound recordings of unknown history very difficult.

A rule-of-thumb for organic materials is that those materials of natural origin or chemically similar to those of natural origin are more susceptible to fungal degradation than are synthetic materials. This seems to be true with the usual exceptions to any rule involving fungi. Some naturally occurring materials (such as the gums of vegetable origin which remain unaffected by many years of soil burial before they are harvested) are very resistant to fungal damage.

Excellent fungi nutrients have been incorporated into many sound records. These include: oils, waxes, cellulose, lignin, fatty acids, some plasticizers, and modified cellulosics. It will be noted that these materials are used as plasticizers, fillers, lubricants, and extenders. The basic resins are fungi resistant with the exception of cellulose nitrate and cellulose acetate; and cellulose acetate is the most resistant of the cellulosics. Many of the packaging materials used in storage provide carbohydrates, proteins, waxes, cellulose and lignins for fungi nutrition.

It would seem that a fungicide is needed, and this approach was studied in this program. A satisfactory fungicide would have to:

(1) Be non-toxic to humans.
(2) Be toxic to a wide range of fungi.
(3) Have a long, useful life.
(4) Not contribute to the degradation of any of the many sound recording material constituents.

Such fungicides are available for incorporation into a plastic during manufacture and it was thought that it might be feasible to incorporate such a material in the jacket or envelope to protect stored discs.

The commercially available fungicides (including those specifically designed for incorporation into plastics) were reviewed in an attempt to find a

material which would meet these requirements. Those compounds containing copper, zinc, chlorinated phenols, and acidic radicals were rejected because of their probable contribution to chemical degradation of some of the disc plastics. Many compounds were rejected because of toxicity or offensive odor. Of the remaining compounds studied, none possessed the necessary quality of slow release of a fungicidal ingredient for a long enough period of time to protect satisfactorily a disc when incorporated in the packaging material (Ref 92 contains excellent discussion of this problem). Fortunately, fungi require an adequate amount of moisture to be active (and destructive) and the other studies had indicated that environmental moisture content should be kept at a level below that required for fungal activity. The fungus problem is, therefore, really just more justification for such environmental moisture content control. The fungi problem is also an additional argument for keeping records clean as most dusts and lints are, to a degree, hygroscopic and tend to maintain a higher moisture level on a surface than would otherwise exist there, and fingerprints serve as good culture media. Other biological agents, such as bacteria and insects, do not seem to be a problem for these materials in library environments.

G. Predicting Shelf Life

A fundamental question in any study such as this one is: What is the potential shelf life of sound record X stored in an environment Y? The only known method of obtaining an accurate answer to such a question is to store sound record X in environment Y and observe the length of time required for failure. This is, of course, an unsatisfactory technique for obtaining the desired answer, and so engineers and scientists have developed techniques for comparing stability or for guessing or estimating potential life of materials. The accuracy of such a prediction is, of course, dependent upon the completeness of knowledge of the material being investigated.

Because of the great lack of knowledge of the degradation behavior of any organic material, the best approximation which can be made for sound recording materials must be couched in such terms as many years, many decades, or more than a minimum length of time. An investigator would not be surprised to find that an organic material whose life he had estimated to be many years was still in good condition many decades or even many

centuries later. He would properly feel concerned about the validity of his work only if the material failed in a few years. It seems only fair to explain this state of affairs to those readers who need such predictions in their work but must either do without them or accept not completely satisfactory ones.

One of the techniques used for the evaluation of life of a material is artificial aging. Artificial aging consists of placing the material in an environment which increases the rate of degradation of the material. Such an environment might provide a greater intensity of ultra violet light, a higher temperature, or a higher concentration of a reactive agent than the material would normally be subjected to. The theoretical basis of artificial aging is quite sound. Briefly, it is based on the fact that the occurrence of an event such as the diffusion of an oxygen molecule to a reaction site, the breaking of a primary valence bond, or the movement of a chain segment of a polymer molecule with respect to the rest of the molecule depends on the random movement of molecules or molecular segments or the acquisition of sufficient energy by an atom to surmount a barrier. Such events occur in accordance with the laws of probability and can be made to occur more often by increasing the concentration of reacting constituents or the energy available to the system.

Practically, however, there are two insurmountable obstacles to obtaining completely accurate results by this technique. First, the chemical and physical deterioration of a material consists of many different kinds of interrelated events which interact on each other. It is impossible to accelerate each of the mechanisms to the same degree so that the natural aging behavior of the material is perfectly imitated. Secondly, the kinds of aging reactions which occur are changed by sufficiently intense changes in reaction time or energy content. It is generally impossible to determine the point at which the proper limits of acceleration have been exceeded.

Accelerated aging techniques are, despite their deficiencies, valuable tools for comparing stability of organic materials and for studying the mechanisms of degradation. The more knowledge that is available about the natural aging of a material, the more information can be gained by such tests.

Another technique which is used for predicting long time behavior is extrapolation. This consists of choosing an index (such as a physical property or the concentration of a chemical in the material) and a limiting value of this index which denotes

failure of the material, measuring the change in value of this index for a period of time, and assuming that the change in value of the index will obey the same rules during the remaining life of the material as it did during the observed period. There is, obviously, no assurance that one has chosen the proper index of failure or that the rules of behavior of this index have been fully outlined during the observed period.

There are other considerations which militate against an investigator who attempts to predict long-time storage behavior of an organic material. There are the differences in formulation, processing, and history of the material which affect its storage life as well as such items as shape and size factors which prevents information gained on the same material in other applications from being completely applicable to the case at hand.

Perhaps the best illustrative example of the difficulties involved in predicting shelf life of a recording medium is that of cellulose nitrate. This material has been in use and chemists have been studying the degradation of this material for nearly a century. (103) Cellulose nitrate motion picture film has been stored under known conditions for about half a century and its shelf life has been studied for a quarter of a century. (125) This investigation has not been confined to one organization, but has been a subject for international research by both government and industry. (123) Despite the background of knowledge resulting from this experience there is no method presently available for determining the potential useful life of such film or even a reliable estimate for the maximum period of time such a film may be safely stored without testing it for signs of incipient failure. On the credit side of the ledger, laboratory tests have been developed which predict incipient failure and preclude loss of the film if these tests are made every one or two years to determine need for copying.

In a study such as this, one cannot dismiss the subject of potential shelf life of sound recordings by merely saying that no such estimate can be made. The fact remains that the librarian must have some basis for determining when to re-record in order to preserve valuable transcriptions. Each year that is added to the predicted shelf life of a record prior to re-recording increases the efficiency of the librarian's operation. There are a number of rational steps which can be taken as a basis for re-recording schedules.

The first step is to set a minimum *known* life expectancy. This is a figure which may (or may not) be far less than the minimum *actual* life expectancy. It is a figure which can be continuously revised upwards as experience with and knowledge of the material increases. One source for such a figure is ready at hand; that is, if a stack survey shows that a certain type of material has been stored without failure for twenty-five years, one can logically assign a minimum known life expectancy figure of twenty-five years to this particular material in this environment. A librarian can use such information to preserve precious recordings by starting with a twenty-five-year re-record cycle for this class of material and can gradually increase the re-record time interval as experience with storage of the material increases. Trivial as this method seems, it was the basis for archival preservation in Germany (125) during a period when valuable records were lost by others due to failure prior to re-recording. This method is expensive and impractical for large collections but it furnishes the first approximation for determining record life.

The next step in determining minimum known useful life is equally simple in concept but is more difficult to apply. That is to improve the figure obtained through observation by correlation or extrapolation. For example, if the minimum known life of material A is twenty-five years and one uses a material B for the same application, which can be proven to have at least thrice the life expectancy of A, one may safely assign a minimum known life of seventy-five years to material B. Another approach to the problem of improving a minimum known life prediction is: (1) establish a value of quality of the recording which is considered satisfactory, (2) from observations determine the probable rate of degradation, over a given interval of time; (3) then from the rate of degradation, we could determine how long the recording would continue to degrade, without falling below the established value of quality. These methods require detailed and complete knowledge of the behavior of the material and each area of ignorance enforces a reduction in predicted life. It is to this step of predicting minimum known useful life that accelerated aging tests are of importance. By combining such tests with analysis of naturally aged materials an investigator, given sufficient time and money, can eventually derive a very accurate estimate of the minimum life expectancy of a material (whether he can keep up with other investigators busily engaged in increasing the stability and life expectancy of these materials is another question).

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After establishing a minimum known life expectancy, two different systems of record preservation may be used. The first is to re-record at the end of this period of time. The second is to begin a testing schedule at the end of this time to determine when re-recording is required. Neither system is entirely satisfactory. The first undoubtedly will result in the loss of many years of useful life and loss of quality of the sound recordings. The second requires the development of an appropriate test, laboratory facilities, and a schedule of testing which must be observed.

To gather the knowledge required to establish an economical minimum known shelf life for sound recording materials together with testing schedules and methods of test for incipient failure would require an effort of many years duration. It would involve an analytical survey of records from many collections and many years of accelerated aging tests. Such a program was too great an undertaking for this project, although it is hoped much of the project work will serve as a logical base for such studies. Because of the need for time, particularly, for accelerated aging studies using moderately elevated temperatures and moderately increased concentrations of reacting agents, such a project would not involve a concentrated effort except in the initial stages of work. The most valuable experiments which could be made could be expected to run for five to ten years with only occasional monitoring. One might question this statement on the basis of the rapid changes and improvements in sound recording media, i.e., to say the materials of today are quite different from those for which the experiment would have been conducted 15 years ago. Nevertheless, it is still believed that we can more accurately assess the longevity of present day records, on the basis of the performance of the older materials, than if no such experiment at all were conducted.

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III. THE STUDY OF PHONOGRAPH DISCS

A. The Acetate Disc

Materials and Degradation Mechanisms

Instantaneous recordings were usually made on discs until this medium was supplanted for this purpose by magnetic tape after World War II. These discs have always had to be designed as a compromise between the requirements of ease of engraving and playback life. This has also involved aging qualities. With the improvement of engraving styli and appurtenant mechanisms, playback life has been constantly improved as the coating material has progressed from soft wax, to ethyl cellulose, to cellulose acetate to nitrocellulose. From the mid 1930's to the present time, such discs have been called acetates and made of castor oil plasticized nitrocellulose lacquer on a metal or glass base. With the exception of the war years, when glass was used as a substitute, aluminum has been the preferred core material.

This type of disc is ideal for the purpose of preparing electroformed matrices* for processing discs and for limited studio use, but has serious disadvantages for library use. However, acetate discs were the best instantaneous recording medium for many years, and so large numbers of these discs form a significant part of many collections. Eventually, if the intelligence on them is to be preserved, they must be re-recorded on a more durable medium, because they do not have an indefinitely long storage life. This is an expensive procedure, however, and it is usually desirable to delay this as long as possible. For one thing, the longer re-recording can be delayed, the more durable will probably be the available medium for transcription.

Cellulose nitrate was the first of the modern plastics, and its invention is often thought of as the beginning of the plastics industry. It is, unfortunately, an unstable material. The most important degradative reactions are thermal, photo-oxidative, and hydrolytic decomposition which result in chain scission or reduction of molecular size. While the decomposition rate is an inherent property of the pure substance, hydrolysis, the catalytic effect of products of degradation, oxygen availability, and the effects of the materials incorporated with the cellulose nitrate all affect this rate. (103) The most significant decomposition product is nitrogen peroxide which is converted into nitrous or nitric acid in the presence of liquid water and, since an acid has a catalytic effect on the degradative reactions, this is an autocatalytic reaction.

The measurement of denitration is used for assessing the stability of nitrocellulose explosives and the deterioration of cellulose nitrate motion picture film while the film can still be duplicated. The same tests as are used for cellulose nitrate motion picture film can be used for acetate discs to determine need for re-recording due to incipient failure caused by degradation of cellulose nitrate. (122, 123)

Unfortunately, the acetate disc formulation introduces an additional problem which is not involved in the deterioration of motion picture film. The cellulose nitrate motion picture film is plasticized with camphor. Camphor is a solvent plasticizer for cellulose nitrate which is not only tenaciously retained by the cellulose nitrate but whose loss by diffusion can be reduced by placing camphor in the film can; plasticizer loss is not a significant degradative mechanism, in this case, because the deterioration rate of cellulose nitrate causes failure while sufficient amounts of camphor are still held by the film.

Castor oil, (103) the acetate disc plasticizer, is a softener (although some of the modified castor oils have solvent properties and are retained much more satisfactorily than raw castor oil) which, in addition, is used in excess to provide a material soft enough for the engraving process. There is such a wide gap between the quantity of plasticizer re-

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*Electroformed copper matrices exhibit surface deterioration during storage, probably as a result of entrapped acid. Nickel matrices, properly made and stored, should have an indefinitely long storage life. This provides an expensive, but feasible, means of preserving valuable recordings.

quired to provide the physical properties needed for engraving and the amount required to provide the properties needed for playback, that a considerable amount of the castor oil can be lost without damaging playback qualities, but the loss of this plasticizer causes shrinkage of the lacquer coating. Because the coating is bonded to the core and cannot shrink, the result is the creation of internal stresses which result in cracking and peeling of the coating.

Castor oil is lost from the acetate disc in a number of ways. It can degrade to form volatile compounds, it can be consumed by fungi, it can exude and diffuse from the material without chemical change, it can be extracted by water, and it can be forced out of the interstices by the action of the attractive forces between nitrocellulose molecules and molecular thermal motion which tend to bring the cellulose nitrate molecules closer together. One phenomenon, noticed in the accelerated aging tests, was the condensing of castor oil molecules into discrete droplets in the plastic which resulted in the formation of "pores" in the disc surface. The odor observed on opening boxes of acetate discs and the oily deposit noticed on the surfaces of stored discs is castor oil (with, sometimes, amounts of compatible plasticizers which are often used with the castor oil). The gradual loss of plasticizer results in progressive embrittlement and, finally, catastrophic failure of the coating. The effects of loss of plasticizer (and, probably, retained solvent) were the only effects which affected playback that were noticed in the accelerated aging tests.

Plasticizer loss and deterioration of cellulose nitrate actually occur simultaneously, of course, and under actual storage conditions, the physical and chemical changes which occur in the coating are the results of the inter-action of both of these factors. The oxidation products of the degradation of castor oil may catalyze denitration of cellulose nitrate, for example, and the loss in strength occasioned by chain scission may hasten failure occasioned by stresses induced by plasticizer loss. Likewise, the agents of degradation affect both parameters. Elevated temperatures accelerate both denitration and plasticizer exudation, for example, while both hydrolysis and plasticizer extraction are induced by excess moisture. The problem posed here is that, in storage, it is desirable to remove the products of decomposition of cellulose nitrate (which requires air circulation) while, at the same time, it is desirable to protect the disc from moisture, oxygen, atmospheric contaminants, and dust (which re-

quires a barrier between the disc and the ambient atmosphere). While it is possible to provide a system which will accomplish both ends (by using a circulating nitrogen system with alkaline scrubbers, for example) such a system is not economically feasible. Where sound recording discs in library storage are concerned, the choice seems to be between using a record jacket which permits diffusion of volatile products of decomposition and a record jacket which is a barrier against water, oxygen, and other gases of the stack environment.

Chemical Analysis to Verify Degradation Theories

If these concepts of the mechanisms of degradation of acetate discs are correct, simple chemical tests can be developed to predict incipient coating failure and a surveillance scheme can be established for preserving acetate discs. Also, the optimum library storage environments are determined by these parameters.

Chemical analysis was used to check the theories of degradation of acetate discs and to determine the feasibility of using chemical tests as indices of degradation. Two specimens were chosen for test:

(1) A glass base disc taken from the Library of Congress shelves which had been made and recorded in 1944. The coating had failed by shrinking, peeling, cracking, and embrittlement.

(2) An aluminum base disc made in 1958 obtained from ordinary commercial sources. This disc was a standard disc whose original formulation differs from that of the old disc by the use of a combination of modified castor oil, alkyd resin, and synthetic plasticizer instead of raw castor oil. (126) Raw castor oil is more susceptible to oxidation, volatilization, polymerization and cross-linking than the modern plasticizer complex.

Despite the difference in formulations, the significant degradative mechanisms should be the same in kind if not in rate.

Nitrocellulose decomposes continuously with time to give various oxides of nitrogen, which in turn react with each other, or with oxygen or water vapor or other materials present in the environment. These gases may cause degeneration in several ways. For example, they may react with water to form nitrous acid (HNO_2), nitric acid (HNO_3), or other acid derivatives of the oxides of nitrogen; these acids, in turn, may act as a catalyst for the degradation of all the constituents

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or they may bring about further polymerization and/or cross-linking of the nitrocellulose and the plasticizer, causing embrittlement. In other instances they may result in removal of HOH from within the molecule or cause mild oxidation, especially to the plasticizer. Finally, they may cause the cleavage of the cellulose molecule itself to produce several organic acids.

The plasticizer can also undergo a number of changes. It may exude or diffuse from the lacquer without chemical change or it may polymerize further and/or cross-link by isomerization, increasing the brittleness of the coating. This isomerization is a result of the shifting of double bonds; therefore, the difference may show in the spectra of the materials. The plasticizer may oxidize to form an epoxy type compound which will cross-link and cause embrittlement. The polymeric chain may also be cleaved by air oxidation or by the action of acid or NO_2. There is also the possibility that lower molecular weight organic acids will be formed from the glycol ester by acid hydrolysis.

The dye may be affected by air oxidation or acid hydrolysis. The other constituents of the lacquer should be relatively stable and inert.

The nitrocellulose coating was stripped from the base of the record. One gram of the material, weighed to the nearest milligram, was placed in a Soxhlet extractor with 90 ml of reagent grade acetone and 10 ml of distilled water* and digested for 1 hour. The apparatus was allowed to cool and the pH of the liquid was determined with a pH meter.

The solutions were evaporated to dryness over a steam bath, care being taken not to bake them. The residue was redissolved in acetone and the material filtered through a Seitz cellulosic pressure filter. Two filter discs were used to obtain good filtration. Approximately 0.2 psi was used on the filter to give a rate of 1 drop every 3 seconds. The color change during the filtration was noted. The spectra in the visible and near-infrared were run on this filtrate in a Perkin-Elmer Spectracord spectrophotometer. (127) The spectrum for pure acetone was subtracted. Forty drops of the filtrate were evaporated on to the sodium chloride optical disc of an infrared spectrophotometer and the infrared spectrum was run. Also, similar spectrograms were run on an acetone solution of the original nitrocellulose coating from the records.

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*Water was used for pH measurement.

The results of the testing of the nitrocellulose records are summarized in Table 3. In almost every test there is a qualitative difference between the new and the aged material. It is quite certain that many of these tests can be developed to give a quantitative measurement of the state of aging of a record. The greater acidity of the aged nitrocellulose is as might be expected from the known production of nitrous acid and various organic acids during decomposition. The extract of the new coating is also slightly acid, which is probably caused by the hydrolysis of some of the nitro groups in the nitrocellulose during the extraction. The difference in acidity can be easily determined quantitatively. The use of two Seitz cellulose filters, in a sense, provided a small chromatographis column in which a noticeable separation of components was achieved during filtration. The characteristic yellowing of nitrocellulose with age is observed in the deeper colors of the initial stages of the filtration and also in the greater absorption at 6,000° A. The dye appears to separate last.

The infrared spectrum obtained from the extract of the record material shown in Figure 2 contains a number of peaks which show a difference between the new and aged records. The measurement of these peaks might well be developed into a quantitative measure of the aging. The decrease in absorption at 3.43 microns shows a loss of methyl groups by the aged material. The decrease in the absorption at 3.53 microns indicates the cleavage of the plasticizer at the double bonds to form separate hydrocarbon groups which are lost by evaporation. Less absorption of 5.79 microns indicates the probable loss of the stearate ester (saturated ester) and conversion of the plasticizer ester to other polymerization products. The broad absorption at 6.0 microns is due primarily to organic nitrates and indicates that the $R-ONO_2$ content of the aged material has definitely been reduced. The reduction of the 6.85 micron absorption band in the aged record further indicates loss of alkyl groups. The separate absorption by the new material at 7.79 microns is due to organic nitrate and substantiates loss of nitro groups from the nitrocellulose as it decomposes. The absorption at 7.83 microns is due to the ester group and the broad band portion is due to the $R-ONO_2$; the reduction in absorption indicated is further evidence of the loss of these two groups from the aged material.

Spectra were also run on the samples of the original material which had been dissolved in acetone but not filtered or otherwise treated. Two addi-

TABLE 3.—RESULTS OF TESTS OF NITROCELLULOSE RECORDS

	Aged	New
Weight	1.0174	1.0762.
pH	4.2	5.1.
Original Color (after digestion)	Blue	Violet.
Pliability	Brittle	Very pliable; bends without breaking.
Filtrate Color, 1 min	White	White.
Filtrate Color, 3 min	Faint yellow	White.
Filtrate Color, 5 min	Golden	Faint yellow.
Filtrate Color, 7 min	Golden red	Grey.
Filtrate Color, 10 min	Red	Red-grey.
Filtrate Color, 15 min	Blue-red	Purple.
Spectrographic Analysis of Filtrate:		
Visible	Strong absorption at 6000 Angstrom units.	Medium absorption at 6000 Angstrom units.
Near-infrared	No significant differentiation	
Infrared	a. Less 3.43 micron absorption	
	b. Less 3.53 micron absorption	
	c. Less 5.79 micron absorption	
	d. Less $6.00 \pm .2$ micron absorption	
	e. Less 6.85 micron absorption	
	f. No 7.79 micron absorption	Separate 7.79 microns.
	g. Considerably less 7.83 micron absorption.	
Spectrographic Analysis of Total Acetone Soluble Material:		
Visible	Considerable 7000 Angstroms absorption	Medium 7000 Angstroms absorption.
Near-infrared	More 17,500 Angstroms	
Infrared	Considerable 2.8–3.2 microns	Medium 2.8–3.2 microns.
Chloroform Solution	Blue color; slowly forms; no plasticizer extracted no 5.75 micron absorption.	Yellow color; quickly disperses; plasticizer extracted; some 5.75 micron absorption.

tional absorption bands were noted by this means. The increased absorption at 17,500° A indicates the presence of more cyclic or cross-linked molecules and that further polymerization of the plasticizer has taken place. The strong absorption at 2.8–3.2 microns in the aged material is due to an increase in the organic acids, especially acetic acid.

The chloroform extraction showed further points of difference. The aged coating releases dye which indicates that the dye has been altered to become soluble as the new coating did not release its dye. The absence of plasticizer in the extract from the old coating shows that the plasticizer which had exuded had evaporated and the remaining plasticizer had further polymerized and was no longer soluble in the chloroform.

Definite and measurable chemical differences exist between the new and old nitrocellulose discs. These differences develop before any outward signs of degeneration or loss in playing quality is manifest. It should be possible to develop these tests to the point where the remaining useful shelf life of a batch of records can be predicted before signs of physical degeneration are apparent. Specific analytical tests which offer promise as indices of incipient degradation are measurements of plasticizer concentration and nitrocellulose denitration. Additional work is required to key these chemical tests quantitatively to the degradation of discs.

Accelerated Aging Tests

The naturally deteriorated acetate disc chosen for chemical analysis provided valuable evidence as to the mechanisms of storage degradation. Alongside it in the stacks of the Library of Congress were discs of similar manufacture and age which are still in good, playable condition. Lacking the complete history of these discs, it is impossible to do other than catalog the manifestations of degradation from a study of them. The determination of the causes of deterioration, the knowledge of which is so essential to establishing techniques for pre-
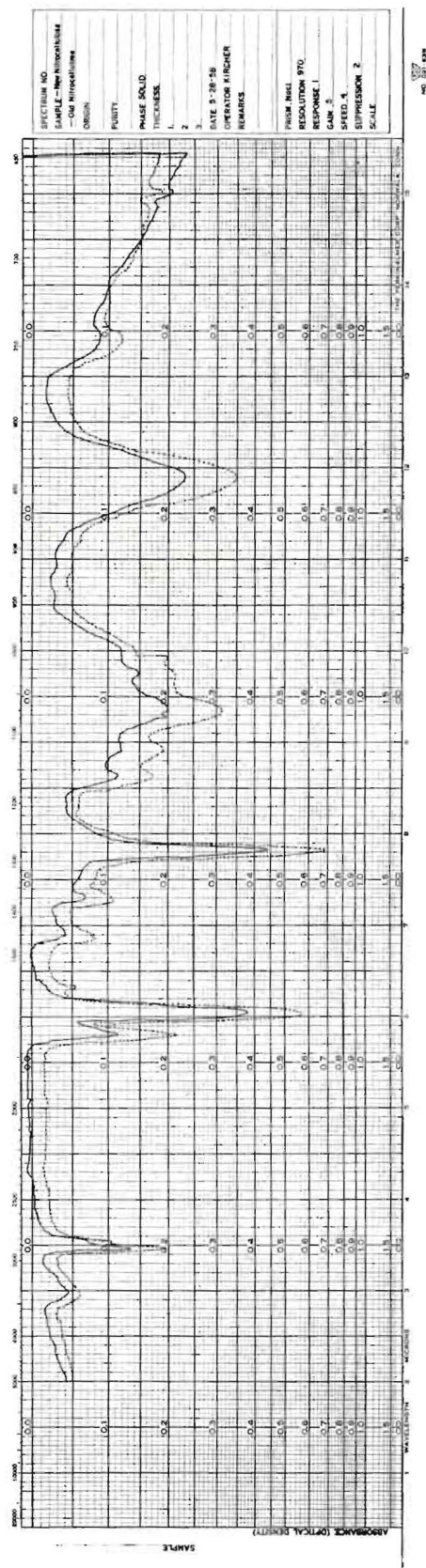
Figure 2. Infrared spectra of nitrocellulose materials.

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venting or inhibiting degradation, involves both linking of cause to effect and the elimination of possible alternate causative factors. In the absence of sufficient information about the natural aging of discs it was necessary to use accelerated aging techniques and to attempt to correlate the results of these tests with the manifestations of aging observed in the stored discs.

The specimens provided by the Library of Congress were regular acetate discs obtained from ordinary commercial outlets. Master discs were 12 in. double faced regulars picked for smoothness of coating. The specimens were as follows:

(1) 12 in. and 16 in. double faced regular blanks.

(2) 12 in. 78 rpm and 16 in. 33⅓ rpm discs precut on both sides with unmodulated grooves at 88, 104, 112, and 120 times per inch.

(3) Standard frequency test discs: 12 in. 78 rpm at 104 lines per inch, 12 in. and 16 in. 33⅓ rpm at 128 lines per inch, all recorded with fixed frequencies of 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 KC.

(4) Constant amplitude test discs: 12 in. 78 rpm and 33⅓ rpm at 96 lines per inch, recorded with fixed frequencies of 50, 100, 200, 300, 400, and 1000 cps.

The first tests made were exploratory in nature. As has been previously noted, laboratory studies of aging of organic materials are based on the work at the Bureau of Standards which began with the study of paper and included work by Hill and Weber (122) on cellulose nitrate motion picture film. Hill and Weber found that aging in a dry oven at 212° F for 10 days produced much the same result for cellulose nitrate film as did natural aging to failure; they also found that deterioration was tremendously accelerated by thermal aging at high humidity in a stagnant atmosphere at 212° F (viscosity measurements indicated that chain scission which obtained in three days at high humidity required thirty days at low humidity).

This temperature proved to be excessive for acetate discs because of the profuse exudation of liquid plasticizer at this temperature which did not cause coating failure but did destroy tonal fidelity. Although other measurements could not be made, significant denitration of the nitro cellulose was indicated after five days' exposure to 212° F in a dry atmosphere by the change in color of light transmitted through coating stripped off of the discs to a green indicating the presence of

nitrous compounds while the coating still maintained its integrity. Exposure to 212° F at 100% humidity resulted in extremely rapid coating failure. Since this temperature was excessive for correlation of results with natural aging, progressively lower temperatures were used until the results obtained were more nearly comparable to the effects of natural aging observed in stored discs. When 150° F had been found to be the maximum temperature to which these discs could be exposed without the occurrence of gross changes not correlable with the manifestations of shelf aging, accelerated aging tests were begun.

These tests consisted of exposing test discs to extremes of temperature and humidity, to cyclic changes in temperature and humidity, and to ultraviolet light. The discs were inspected for changes in lacquer coating weight, appearance, and continuity as well as for changes in playback fidelity. The equipment used for accelerated aging tests and inspection as well as the techniques of inspection are presented in the Appendix of this report.

The purpose of these tests was to determine what changes in playback quality result from the chemical and physical changes which occur during shelf aging and to correlate these changes with environmental factors. This required the reproduction of the manifestations of shelf aging within the time alloted for testing.

It became apparent during testing that presently made acetates are far more resistant to chemical deterioration than had been expected and that using unmodulated groove and sine wave test frequencies produced somewhat unrealistic results because the stylus, during playback, wiped out the irregularities in the groove walls caused by aging. It appears that quantitative tests which could be used for prediction of life under normal conditions would require the use of more complex wave forms (such as are actually used in music and speech records) and much longer exposure times (of the order of five years) to milder aging conditions (maximum temperature 100° F). It also seems evident that there is sufficient difference in the stability of modern and obsolete lacquer formulations to justify separate consideration of the two types of discs.

The biggest difference between these two types of discs seems to be in stability and retention of plasticizer. While no new specimens of the old formulation were available for testing, chemical reasoning indicates that raw castor oil is quite susceptible to oxidation (as was noted in the chemi-

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TABLE 4.—RESULTS OF ACCELERATED AGING OF ACETATE DISCS

1. Constant Temperature and Humidity Tests

Discs Tested*	Temp	Time	Humidity R.H.	Air	Results
2–AX and 2–AY	120° F	1 mo	>90%	Circulating	Noise+4 db.
2–BX and 2–BY	135° F	1 mo	>90%	Circulating	No chg in freq or distortion; some coating failure.
2–AX and 2–AY	150° F	1 mo	>90%	Circulating	Noise+7 db.
4–BX and 4–BY	150° F	1 wk	>90%	Stagnant	Coating failure.
2–AX and 2–AY	120° F	1 mo	>90%	Stagnant	Coating failure.
2–BX and 2–BY	150° F	1 mo	<10%	Circulating	No chg in freq or distortion.
2–AX and 2–AY	150° F	1 mo	<10%	Stagnant	Noise+7 db after removing oil.

2. Constant Temperature with Humidity Changed Each 24 Hours—Air Circulating

Discs Tested*	Temp	Time	High Humidity	Low Humidity	Results
2–AX and 2–AY	120° F	1 mo	90%	10%	Noise+4 db.
2–AX and 2–AY	150° F	1 mo	90%	10%	Noise+7 db.
2–BX and 2–BY	150° F	1 mo	90%	10%	No chg in freq or distortion.

3. Constant Humidity with Temperature Changed Each 24 Hours—Air Circulating

Discs Tested*	High Temp	Low Temp	Time	Humidity	Results
2–AX and 2–AY	120° F	−40° F	1 mo	10%	No change.
2–BX and 2–BY	120° F	−40° F	1 mo	10%	No change.

4. U.V. Exposure Only

70° F, 50% R. H., 2–BX for 1 mo, no change in frequency, distortion or noise.

*A—unmodulated groove disc.

B—test frequency disc.

X—new disc.

Y—new disc exposed to 24 hours ultraviolet light before test.

cal analysis discussion) and volatilization. Specimens of the new formulation were subjected to accelerated oxidation tests* but no evidence of

*This test consisted of placing specimens in an oxygen bomb (a closed stainless steel pressure vessel) with an atmosphere of pure oxygen at 100 psi pressure. This bomb is placed in a constant temperature water bath and is connected to a recording pressure gauge. Reaction between specimen and oxygen is indicated by specimen weight changes, drop in pressure during test, or changes in specimen properties. The acetate specimens were exposed to 100 psi of oxygen at 120° F for periods of 24, 100, 250, and 750 hours with no measurable oxidative reaction occurring. A.S.T.M. D572–48 depicts an oxygen bomb of the type used in this test.

oxidation was noted. In addition, the loss in weight after exposure at 212° F, 0% R.H., in circulating air, for two weeks corresponded to a loss of only 25% of the castor oil in the coating which is a much smaller loss than would be expected from the old formulation. It is realized that these tests are far insufficient, both in scope and measurement of parameters, to provide a scientific basis for an adequate theory of the degradation of acetate discs. They do, however, provide quite a bit of useful information; this information, when correlated with the observations of others, gives an indication of what can be expected from these discs.
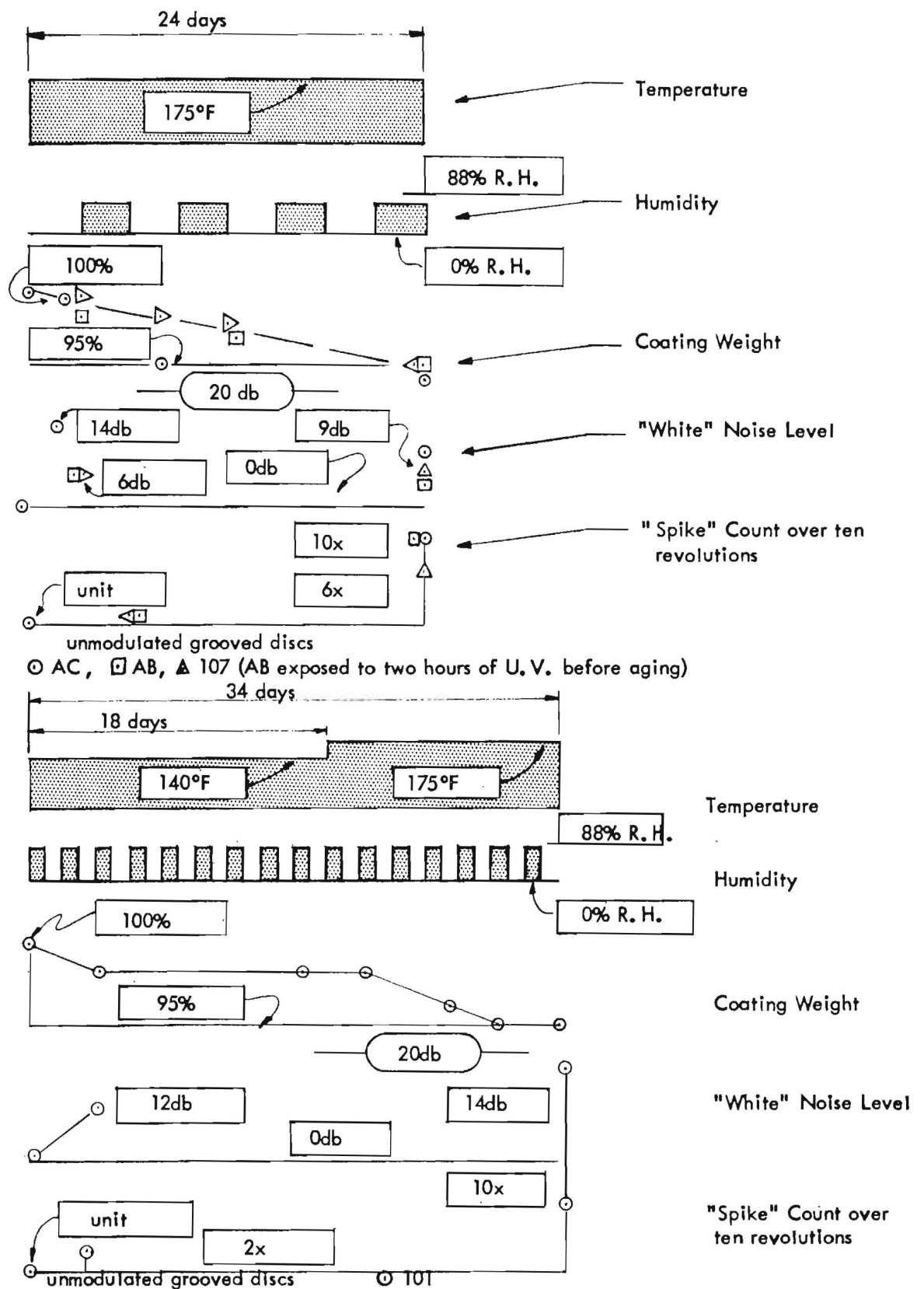
Figure 3. Results of accelerated aging of unmodulated groove acetate discs.
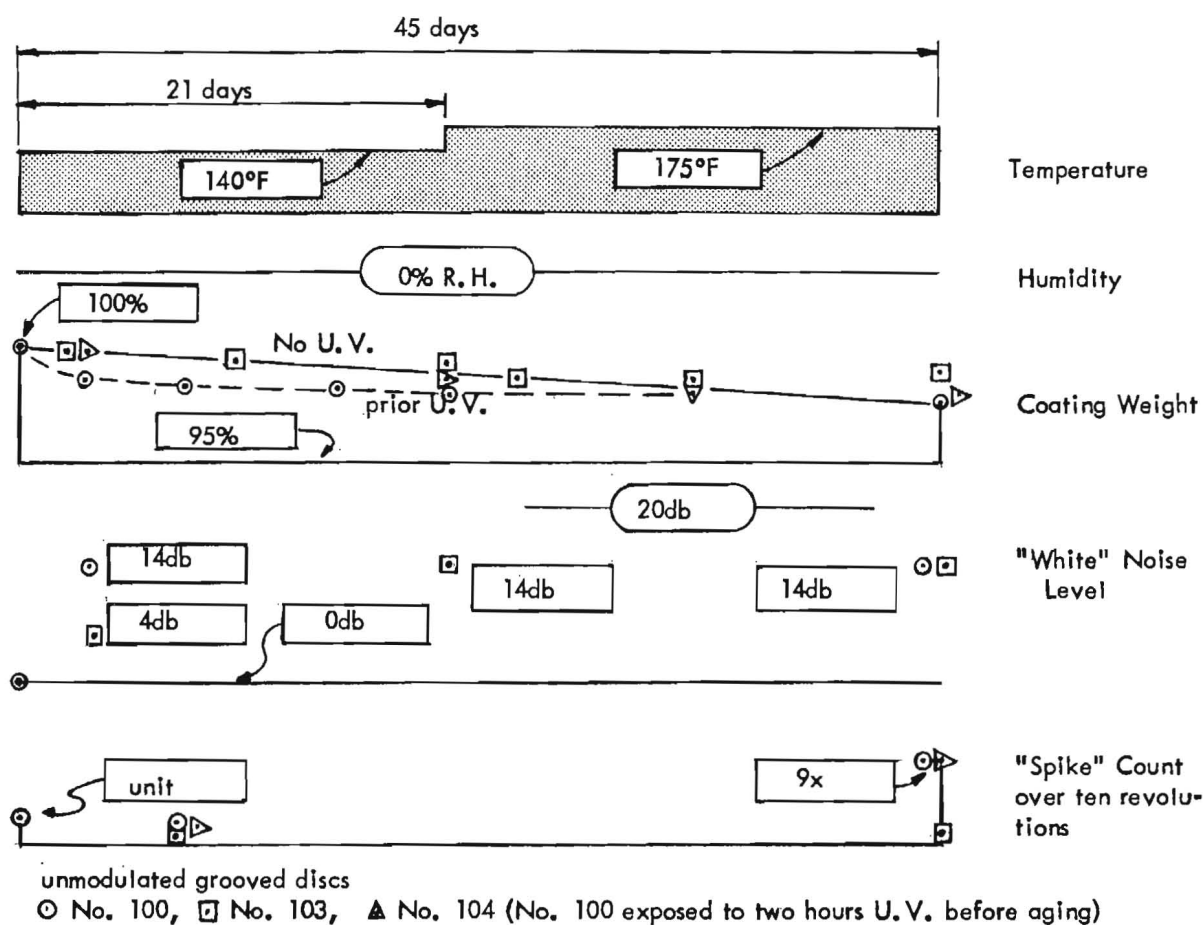
unmodulated grooved discs
⊙ No. 100, ⊡ No. 103, ▲ No. 104 (No. 100 exposed to two hours U.V. before aging)

Figure 3. Results of accelerated aging of unmodulated groove acetate discs—Continued.

Observations Regarding Aging

Latham (63) and others have observed that acetate discs "dry out" or lose plasticizer during the first part of their shelf life and that this is manifested by an increase in noise but no other observed changes in fidelity; in addition, this is the only manifestation of aging observed in 15 years' histories of these discs (except for occasional and erratic coating failures). This is also the only manifestation of aging observed in the tests and, furthermore, the magnitude of the increase in noise is the same as was observed by Latham in shelf aging. Microscopic inspection of the discs indicate that this increase in noise is probably occasioned by the shrinking of the coating which exposes small nodules of imperfectly dispersed carbon black or other solid material as well as by the formation of minute pores due to exudation of plasticizer. The plasticizer is incorporated into the new disc in such excess that about 25 percent of it may be lost without serious damage to the playback qualities of the disc. Oxidation and denitration do not seem to play a significant role in this manifestation of aging.

The final manifestation of aging seems to be catastrophic failure by loss of coating continuity and by delamination. While this has in some instances been observed to occur in less than 15 years, such occurrence is so erratic that it is presumed to result from poor fabrication or exposure to fungal attack or extremes of temperature and humidity. In longer time storage, both plasticizer loss and chemical degradation of cellulose nitrate recordings, embrittlement so serious that it prevents successful replay may precede coating failure; the possibility of this happening cannot be determined from these tests. The potential longevity of these discs is probably somewhat less than that of cellulose nitrate motion picture film (which is of the order of half a century) (123) both because of the plasticizer used and because a low viscosity cellulose nitrate (with less inherent stability) is probably used in most lacquer formulations.

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In years, under ordinary storage conditions, the well-made discs of the older formulations have a minimum *known* life expectancy of about 15 years. This figure was obtained from the inspection of discs stored by the Library of Congress under the environmental conditions previously outlined as well as the experience of the USN Underwater Sound Laboratory (63) and others. Modern discs should have a longer life than these specimens. Even the modern discs, however, cannot be considered to have indefinitely long shelf lives because of the known instability of the material (103) (123) and must eventually be re-recorded if the intelligence on them is to be preserved. The differences which exist between acetate discs caused both by fabrication and environmental history rule out the use of chronological age as a criterion for prediction of failure, and the development of simple chemical analytical tests is recommended.

B. The Shellac and Shellac Type Disc

General

The shellac and shellac type formulation is used for pressing normal groove discs. Of historical interest are the shellac laminates which consisted of a structural core made of such materials as cardboard or a thermosetting resin coated with a soft shellac-wax material into which the grooves were pressed. This is not an efficient process, however, and it was early supplanted by a molding compound consisting of an aggregate (such as wood or rock flour) bound together and protected by synthetic or natural resins and waxes. Since shellac was the only thermoplastic resin available, at the time, which would withstand molding temperatures, it was used in the pressing of the first such discs and its excellent properties assured its continued use until the normal groove disc was supplanted by the microgroove disc for quality sound recordings. Even during the period of shellac dominance as a binder material, however, the vagaries of the shellac market resulted in the use of other resins by many manufacturers. At the present time, normal groove discs use such materials as Vinsol, Valite, vinyl chloride-acetate, and other commercial resins for a binder instead of shellac. It is, unfortunately, often difficult to distinguish between shellac and shellac type discs by inspection, and even most quality disc manufacturers extend shellac up to 200 percent with materials of inferior aging qualities. This, together with the wide variety of formulations and

ingredients used, make it almost impossible to make any statement about these discs which would be valid for all such discs found in a single collection.

Nevertheless, libraries have important collections of normal groove discs whose preservation is important. Many of these discs have survived for half a century and appear to be still in excellent condition, while some of them have deteriorated in less than a decade. It is hard to determine the cause of this degradation in most cases. In ordinary environments, storage stability of cellulosic flours and fibers ranges from good to terrible, of clays and ground slate from excellent to good, and mineral flours generally are rated as excellent. Likewise, the waxes of vegetable and mineral origin exhibit a wide variation in stability as do the resins used as extenders or substitutes. All of these materials are most sensitive to environmental factors.

Laboratory Investigations

Three typical formulations were chosen for study in this program. The shellac formulation studied was:

Flake Shellac.................. 15.63% by weight.
Congo Gum................... 6.51% by weight.
Vinsol Resin.................. 5.86% by weight.
Carbon Black (low oil content).. 2.61% by weight.
Zinc Stearate.................. 0.32% by weight.
Whiting ($CaCO_3$ passing #400 52.13% by weight.
  mesh).
Aluminum Silicate (passing #400 13.03% by weight.
  mesh).
Flock (long fiber).............. 3.91% by weight.

In addition, two shellac type formulations (D & E of the fungus study) which used crushed limestone as aggregate and vinyl chloride-acetate or resins obtained by the destructive distillation of wood and other cellulosic materials were studied.

Two factors contribute to the dimensional stability of all discs of this type. First is the aggregate which reduces the thermal coefficient of expansion of the material as well as providing added strength. Second is the greater thickness of these discs. Dimensional stability is often impaired by the sensitiveness of some of the aggregates to moisture and the loss of waxes and oils which occurs during aging.

No elaborate tests were made on these discs because it was felt that the results thereof would not be applicable to a collection of discs. They were exposed along with the plastic discs to fungal action (see Fungus Study), elevated temperature, high humidity, and cyclic variations of temperature and

humidity for one month periods. The shellac type formulation of crushed limestone and vinyl chloride-acetate proved just as stable as did the unfilled vinyl chloride-acetate discs (see Plastic Disc, Section C) and exhibited greater dimensional stability. The inferior shellac type formulation proved to have good dimensional stability but displayed random embrittlement when exposed to high humidity and temperature environments. This latter formulation also was quite susceptible to fungal attack.

The shellac disc was studied in somewhat more detail than the shellac type discs. The first test made was to determine the state of "cure" of the shellac. "Cured" shellac has both thermoplastic and thermosetting properties, and the degree of each type of behavior exhibited by a given sample is a function of completeness of "cure." Raw shellac is a solid solution of a number of organic compounds and reacts to an applied stress as does a very viscous liquid. During processing and aging, the condensation reaction between the organic compounds results in an increase in average molecular weight and cross-linking between molecules. The reaction is called "curing."

The physical properties of raw shellac and completely "cured" shellac are quite different. The most important of these properties, as far as phonograph discs are concerned, are elasticity and brittleness. Raw shellac is easily deformed and flows readily. Completely cured shellac deforms far less readily, is much more elastic, and is much more brittle. In addition, the "curing" process results in a denser resin which means that the "curing" process involves shrinkage of the material.

This condensation reaction appears to be the most important aging mechanism of the shellac in these discs. It is an internal reaction of the material and its rate is a function of storage temperature, storage humidity, and completeness of "cure."* A semi-quantitative measure of "curing" is the solubility of shellac in alcohol. Raw shellac is completely soluble, completely "cured" shellac is insoluble, and the extent to which condensation has proceeded determines the degree of solubility of a shellac. The shellac of the test discs proved to be completely soluble in alcohol and became

insoluble after thermal aging. It was concluded that the shellac in newly pressed discs approximates raw shellac in degree of condensation.

From a qualitative standpoint, this means that:

1. Since raw shellac behaves as a viscous liquid and exhibits but little elasticity, there can be no significant internal stresses or strains in a freshly pressed shellac disc.

2. As this condensation reaction proceeds in a stored disc, the disc will become less resilient and more brittle.

3. Freshly pressed discs can be easily warped and straightened, but aged discs, because of the cross-linking, will resist both warping and straightening.

4. There will be some dimensional changes during aging, but, because of the high percentage of filler, these will probably be minor changes.

In order to check these hypotheses, a group of simple laboratory experiments were made.

1. New discs were placed horizontally on a plate in a chamber alongside new vinyl discs and the temperature of the chamber was gradually raised to the softening point of the material (gauged by placing a disc in the off-vertical position and observing the temperature at which it warped from gravity loads in less than 15 minutes). The vinyl discs warped as shown in Figure 15 but the shellac discs did not.

2. The temperature of the discs was raised to and maintained at 150° F for one week. At the end of this time, the discs were removed and compared with new discs. The material of the aged discs was stronger, but much more brittle than that of the new discs.

3. A group of new shellac discs were intentionally warped by gravity loads applied by clamping the discs in a jig. Some of these warped discs were aged in the jig at 120° F and 100 percent R.H. for one week while the others were kept at room temperature. At the end of this period all of the discs had the same amount of warp and they were then placed horizontally on metal plates in a chamber in which the temperature was gradually raised to 120° F. The shellac discs which had not been aged were perfectly flat by the time the chamber came to temperature while the artificially aged discs retained some of the initial warp even after several hours exposure.

4. No noticeable changes in fidelity were observed to result from the mild acceleration of aging possible with these discs. Extreme conditions of temperature and humidity resulted in quick failure of the material by embrittlement.

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*All other things being equal, the rate of a reaction is a function of the concentration of potential reacting elements. In this case, each condensation reaction which occurs reduces the concentration of potential reacting elements and thus the reaction rate for this internal reaction decreases exponentially as the reaction proceeds.

5. These discs proved susceptible to fungal attack, this is probably due to the nutriment furnished by the organic materials other than shellac as the literature indicates shellac is fungi resistant.

A study of shellac formulations indicated that it would be useless to attempt to undertake any quantitative study of the properties of new or aged shellac discs because there is no such thing as a "typical" shellac formulation. Most popular discs made prior to World War II are usually classified as shellacs, and these discs have only one thing in common; they consist of a large amount of aggregate with a small amount of a natural or synthetic cementing agent. If one assumes that most of these discs contain shellac, one is still faced with the fact that shellac varies tremendously in its properties and that it often comprises only one-third of the actual cementing agent used. In addition, the disc properties are as much a function of the filler as they are of the cementing agent and the fillers used run the gamut of natural cellulosic materials as well as of minerals. Of twelve old "shellacs" taken from the shelves of the Library of Congress for study, three of them contained no shellac at all; three contained 12 percent by weight of shellac with a mixture of 15 percent of other resins and gums; and the composition of the other discs is unknown.* This variation in composition was due to both experimentation on the part of manufacturers and the fluctuations of the shellac market.

One cannot, therefore, expect consistent behavior of stored shellac or shellac type discs. In general, they seem to have long storage lives if properly protected against the deleterious effects of moisture, heat, oxygen, fungi, and stress. The major differences between shellac and the vinyl shellac type formulations, as far as storage is concerned, are:

1. Shellac discs are far more subject to damage by moisture (moisture increases the condensation reaction rate).

2. The extenders and modifiers used with shellac are far more susceptible to fungal damage than is pure vinyl.

3. The reaction rate of the major mechanism of chemical degradation of shellac decreases as the reaction approaches equilibrium while the corresponding reaction rate of vinyl is self-catalyzing. This indicates a slow, progressive embrittlement of the shellac disc as a mode of failure in a good storage environment as opposed to the increasingly

*From correspondence with disc manufacturers.

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rapid embrittlement of a vinyl disc at the end of its storage life. The behavior of the other formulations is completely unpredictable, and it can only be hoped that the very unstable formulations form but a small portion of any collection of discs. The only surveillance scheme which seems to be applicable to these discs consists of using skilled judgment to determine when a disc has become so embrittled that it should be re-recorded. Such embrittlement is often noticed by the decrease in flexibility of a disc or by playback (with good equipment) resulting in disc wear so serious that the powder will dirty a soft white cloth wiped across the surface.

C. The Plastic Disc

Materials

The long playing (or microgroove) plastic disc cannot be regarded as just an improved shellac type disc in a study of the storage and preservation of sound recordings. The shellac type disc is made of 70 percent or more of a mineral or cellulosic aggregate which is bound together and protected by resins and waxes. The nature of the binder is important in determining the physical properties and response to aging of these discs, but these qualities are more dependent on the other constituents than on the binder. The plastic disc is made of a thermoplastic into which no more than 25 percent of a filler or extender may be added for the purpose of decreasing the cost of the disc. The resin is all important in determining the physical properties and response to aging of these discs although their quality and storage life may be impaired by the use of fillers and extenders.

Plastic discs are made of polyvinyl chloride or polystyrene. Production costs of injection-molded polystyrene discs are lower than those of compression-molded polyvinyl chloride discs for large runs, but require a larger initial capital outlay. At present, polystyrene represents but a small proportion of the total stored disc population and was not studied in this program. A cursory comparison of the two materials indicates that the same storage environments and techniques which are recommended for polyvinyl chloride discs are indicated for polystyrene discs. The polyblend used for styrene discs seems to be somewhat more susceptible to oxidative degradation than the copolymer used for vinyl discs. At present, indications are that styrene will become a more common disc material in the future
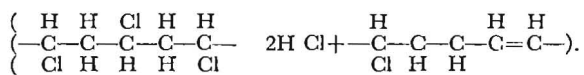
Polyvinyl chloride (PVC) is a synthetic resin which has been commercially produced in the United States for about 25 years. In the sound recording industry PVC is used in the manufacture of phonograph discs, magnetic tape backing, and magnetic tape binder. PVC is used as a binder in 78 RPM shellac type discs and for the manufacture of long playing (L.P.) plastic discs.

Figure 4 depicts a segment of the PVC molecule. The basic unit of this molecule is shown between dashed lines and the number of these units in one molecule (or η, the degree of polymerization) is usually of the order of 1000 or 2000. The long chain PVC molecules are randomly oriented, curled and intertangled together to form the plastic. The individual molecules are not bound to each other by primary valence bonds (except when cross-linking occurs as a result of aging) but by relatively weak intermolecular forces. These forces are too great to provide a plastic having the exact physical properties required for the desired application, and internal plasticization is used to provide a resin whose properties are satisfactory for the pressing of L.P. discs. This is accomplished by copolymerizing vinyl acetate with the vinyl chloride using a mass ratio of about 15 to 85.

Polyvinyl chloride degrades chemically when exposed to ultraviolet light or to heat. (84) (86) (87) (91) (105) (109) (111) Phonograph discs need not be exposed to direct sunlight or other UV sources but they are exposed to heat in both processing and storage. Thermal degradation begins as dehydrochlorination which forms double bonds

$$\begin{pmatrix} H & H & Cl & H & H \\ -C-C-C-C-C- \\ Cl & H & H & H & Cl \end{pmatrix} \quad 2H\,Cl + \begin{matrix} H & & H & H \\ -C-C-C-C=C- \\ Cl & H & H \end{matrix}).$$

The first HCl molecules are probably lost because of impurities or the deviations from theoretical PVC molecular structure which occur in actual polymers and progressive dehydrochlorination is activated by the double bonds in the chain. The double bonds are sites for oxidative attack and cross-linking. Cross-linking is the binding of adjacent chain molecules together by primary valence bonds and is manifested by embrittlement, warping and cracking. The free hydrogen chloride evolved is a uni-
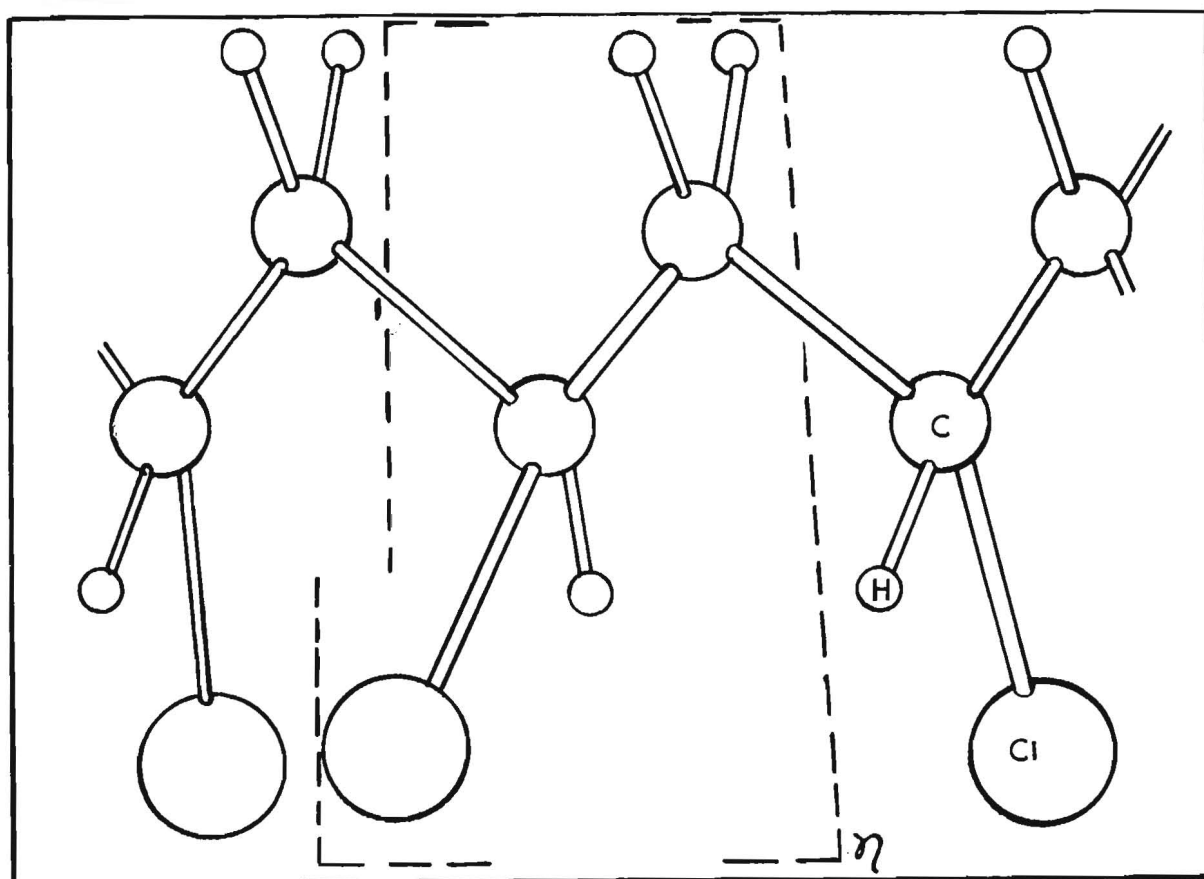

Figure 4. PVC molecule.

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form catalyst for further dehydrochlorination so that a chain degradative reaction results (unless HCl is removed from the system). At processing and molding temperatures, the dehydrochlorination reaction rate becomes so rapid that PVC is noticeably degraded at the end of the molding cycle unless it is properly stabilized. Stabilization is accomplished by adding a chemical to the resin which does not prevent the degradation but controls it mainly by consuming the free HCl evolved. Sufficient effective stabilizer remains in a plastic phonograph disc to protect it for a very long time after pressing. In fact, the reaction rates are so slow that no discs were found in the examination of stored discs which had failed by chemical deterioration.

Study of Aging by Chemical Analysis

Chemical analysis was used to study the internal chemical reactions of vinyl discs. For this purpose, vinyl discs of identical formulation were obtained; an old disc pressed in 1949 and in excellent condition and a newly pressed disc. The discs were made of unfilled vinyl chloride-acetate copolymer with carbon black serving as a pigment and light stabilizer. The vinyl chloride-acetate copolymer decomposes in a number of ways which should leave chemical evidence. An initial decomposition stage is dehydrohalogenation in which the H and Cl are stripped off with the formation of HCl. In a similar manner, the acetate groups may also be removed. These acids are also formed in the first stage of hydrolysis. Further hydrolysis may yield olefins, cyclic compounds or aromatic compounds. Air oxidation may bring about the formation of epoxy-type polymers which are easily crosslinked to form brittle products. Oxidation of the long chain polymer in the middle of the chain may give ketones; and mild oxidation of straight chains may give alcohols. Tribasic lead sulfate was used as a stabilizer for the vinyl plastic to neutralize the free acids and lead stearate was used as a lubricant and secondary stabilizer.

Samples of the vinyl discs were crushed and 3 grams of the material, weighted to the nearest milligram, were placed in a Soxhlet extractor with 90 ml of reagent grade acetone and 10 ml of distilled water,* and digested for one hour. The

apparatus was allowed to cool and the pH of the liquid was determined with a pH meter and then the samples were evaporated almost to dryness. A small quantity of the residue was removed on a spatula and the physical appearance was observed. Comparative melting points were observed by heating the material on the spatula. The heating was continued and the flame color, smoke, and residue were observed. The residues were dried in an oven at 110° C for 15 minutes and weighed and the odor observed. The weight of this residue was then calculated as percent of water soluble material in the record. The residue was redissolved in 100 ml of acetone and filtered through the Seitz filter to remove the carbon black and lead salts. The filtrate was evaporated over a steam bath, then dried in an oven at 65° C for 30 minutes. This residue was dissolved in chloroform and an infrared spectrum run.

The results of the testing of the vinyl chloride-acetate records are summarized in Table 5. As with nitrocellulose records, there are definite differences between the old and new records in every case. Because the mechanisms of degradation are different, some of the trends in the data are in the opposite direction but are subject to reasonable interpretation. The acids liberated in the decomposition of the vinyl plastic must be thoroughly scavenged by the lead stabilizers as the pH of the old material is higher than that of the new. The low pH of the extract of the new record is probably due to the hydrolysis of some of the lead salts.

There are indications from the physical examination of the extract residue that the material from the old record contains considerable aromatic matter. The orange sooty flame and the phenolic smell are indicative of aromatic character, whereas the yellow, clean flame and the odor of palmitic acid would indicate straight chain hydrocarbons. It is well known that vinyl polymers undergo loss of H and Cl to leave unsaturated bonds. It is possible to postulate the formation of aromatic compounds by a ring closure involving these bonds. The palmitic acid could be formed easily by the beta oxidation of the stearic acid formed from the lead stearate.

The infrared spectra of the two materials shown in Figure 5 may furnish the most accurate basis for establishing a quantitative measure of the degree

*The use of the mixture of acetone and water has certain advantages over the use of either solvent alone. Water alone would do little extracting of the vinyl copolymer; acetone alone would not be a good medium for measuring pH. Acetone would dissolve the vinyl plastic and make the separation of the individual constituents more difficult. With the mixed solvent, water soluble materials are separated without dissolving the vinyl and dispersing the carbon black and lead salts.

TABLE 5.—RESULTS OF TESTS ON VINYL CHLORIDE-ACETATE DISCS

	Aged Record	New Record
Weight	1. 2.8835 g 2. 3.3308 g 3. 4.1495 g	2.3572. 3.3408. 4.1646.
pH	1. Lost 2. 6.85 3. 6.85	5.4. 5.5. 5.7.
Physical Properties of H_2O Extract:		
Appearance, consistency	smooth, waxy	gelatinous, gritty.
Color	salmon pink	pale yellow.
Odor	aromatic	slightly sour.
Melting point	slightly above room temp	somewhat higher than aged record.
Flame color	orange	yellow.
Smoke	sooty	none.
Residue	very slight, white	small amount, white.
Odor after drying	phenol	palmitic acid.
% H_2O Extract	2.7	4.8.
Infrared Absorption	more 3.33 micron. considerably more. 3.45 micron. considerably more. 3.55 micron. considerably more. 5.75 micron. considerably more. 5.83 micron. more 7.00 ± .2 micron. more 7.30 micron. more 7.55 micron.	more 8.23, 8.27 micron. with separate fingers. more 12.7 to 13.2. micron absorption.

to which decomposition has taken place, but its utility is probably restricted to research analyses. The absorption at 3.33 and the broad band absorption at 7.0 indicates that the old sample contains more olefins than the new material and substantiates the other indications of increasing unsaturation. The increase in absorption at 3.45, 3.55, 7.30, and 7.55 microns denotes an increase in alkyl groups from further polymerization and cross-linking of the aged vinyl copolymer and the formation of oxidation products. The absorption at 5.75 microns is due to esters. The acetate ester is present in both, but the loss of HCl would tend to increase the proportion of the acetate. Also, additional esters may be synthesized from the decomposition products. The increase in the absorption at 5.83 microns by the old vinyl shows the presence of carbonyl groups. The carbonyl group is known to be present during the second stage of oxidative degradation, and this absorption band might well serve as an indicator of the condition of the records. The greater absorption by the new material at 8.23, 8.27, and 12.7 to 13.2 microns is due to the presence of a greater amount of organic chloride. It is evident this reaction may be the primary degradation that is taking place.

These experiments justify the conclusion that a promising index of the chemical degradation of PVC discs is the determination of free HCl and ionic chloride and that a simple analytical technique (111) analogous to the alizarin red technique for nitrocellulose motion picture film (123) could be developed to determine degree of degradation.

Exploratory accelerated aging tests, using the equipment and techniques described in Appendix A, were used in an attempt to determine fidelity changes induced in vinyl discs by chemical degradation. No change in signal or noise was found to result from prolonged exposure to aging environments which did not induce failure of the
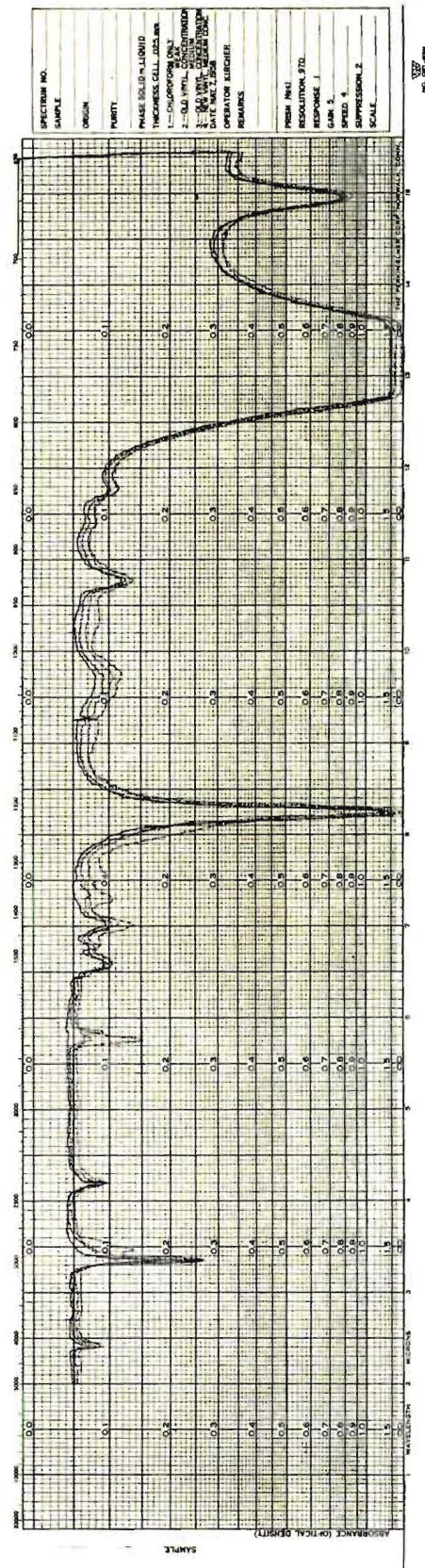
Figure 5. Infrared spectra of vinyl materials.

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disc from other causes.* When the exploratory tests failed to reveal significant chemical degradation within the limits of acceleration permitted by other parameters, a theoretical analysis of degradation rate was made using information available from the literature (105) (111) as well as information provided in private communications from manufacturers of the basic polymer. This analysis demonstrated that significant physical changes caused by internal chemical reactions would require several years of accelerated aging to be measurable and so further aging tests were not made.

Available information** indicates that, for the best formulations, the resin will not be seriously degraded until after the stabilizer is no longer 100 percent effective and that, since the degradation reaction is catalyzed by free HCl, the potential life of a disc can be assumed equivalent to the life of the stabilizer. Neglecting the effects of irradiation and extrapolating the results of accelerated aging tests made by others, *failure by chemical degradation of a vinyl disc in ordinary library environments should not occur in less than a century.* This potential life can be doubled by storage at 70° F. The actual potential storage life with respect to chemical degradation of an individual disc is dependent on its exact formulation (including both kinds and amount of stabilizer and extender used) and its thermal history prior to acquisition (including processing and molding). Apparently, small changes in these parameters can change the potential storage life with respect to chemical degradation by several decades of years. For these reasons, *it appears that a surveillance procedure of inspection and test based on stabilizer exhaustion is the most feasible means of determining need for re-recording of these discs.* The development of a satisfactory surveillance procedure was not accomplished in this project, and is recommended for future investigation. Basically, it would be modeled on the surveillance technique presently used for motion picture film (123) and a simple microanalytical technique based on the work of Wartman (111) and Druesedow and Gibbs (105).

Physical Deformation Induced by Storage Conditions

While no discs were found in either stack surveys or exploratory testing which had suffered appreciable chemical degradation, a considerable number were found which were so warped and deformed that they were no longer playable. An investigation of the causes of this behavior of plastic discs was made to provide a better understanding of this problem *which seems to be of far greater significance in the storage degradation of plastic discs than is chemical deterioration.*

All materials subjected to a continuous load develop a permanent deformation whose value increases with time. For thermoplastics the magnitude of this deformation is so great that their useful application is very limited. For stored discs, creep due to gravity loads can result in both surface imprint which might impair fidelity by local deformation of the groove walls or so warp the entire disc that it cannot be played. Insufficient information was available to estimate the significance of creep due to gravity loads during long time storage and so a series of tests was necessary to obtain the requisite data.

The mechanical behavior of high polymers is usually studied by means of an analytical approach at the structural level of aggregation. That is, a theoretical concept of the structure of the material is developed from laboratory tests and this concept is used both to explain and to predict the behavior of the material. The material is considered to consist of a continuous but nonhomogenous system formed of elements of different properties and finite dimensions whose behavior can be approximated by a mechanical (or mathematical) model. The validity of the concept (or model) is judged by the accuracy with which it can be used to predict the behavior of the material. In a model analysis of high polymers in the transition and rubber-like regions, the knowledge of the internal structure is sufficiently complete to allow the actual identification of each element of the model with a molecular process. This has permitted investigators in this field to develop techniques for predicting the mechanical behavior of high polymers which find no counterpart in the mechanics of other materials.

The simplest system is that of the thermoplastic, such as PVC, whose basic structural element is the long chain molecule which is randomly oriented,

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*For example: (see Acetate Disc Section for Equipment and Techniques) (1) Unmodulated groove vinyl discs exposed to ultraviolet radiation for 275 hours showed no change in weight or groove noise. (2) Vinyl discs exposed to temperatures greater than 120° F warped so much as to become unplayable with no observable change in material. (3) Test frequency and unmodulated groove discs exposed to temperatures of 120° F for 1000 hours showed no change in weight, groove noise or signal.

**Based on tests in which the resin has been exposed to far worse environmental conditions than are phonograph discs, which should provide a conservative estimate.

coiled, kinked, and intertangled. The combination of strong intramolecular bonds and weaker intermolecular bonds causes the strain response to a stress to be a combination of elastic deformation and viscous flow (viscoelastacity). If such a material is linearly viscoelastic and can be considered to be incompressible, the analysis is particularly simple. The laboratory investigation of disc warp due to creep from gravity loads consisted of the following steps:

(1) Measurement of Poisson's Ratio to determine if incompressible deformation can be assumed.

(2) Measurement of linearity of strain response to stress.

(3) Measurement of creep constants.

(4) Analysis of results and estimate of creep induced warp under library storage conditions.

The measurement of Poisson's Ratio was accomplished by the technique described by Timoshenko. (20) A specimen (2.00 in. x 0.50 in. x 0.034 in.) was cut from a 12-in. blank of a typical vinyl disc. This specimen was press polished and then placed in a jig which applied a uniform moment at the two ends of the specimen. A 45° optical prism was then placed at the center of the specimen. A monochromatic source of light was directed normal to the specimen surface and the reflection of the interference lines in the prism was photographed. (See Figure 6.) The photograph was enlarged, the angle measured, and Poisson's Ratio computed. Values measured ranged from 0.43 to 0.45 with an average of 0.44. For a real
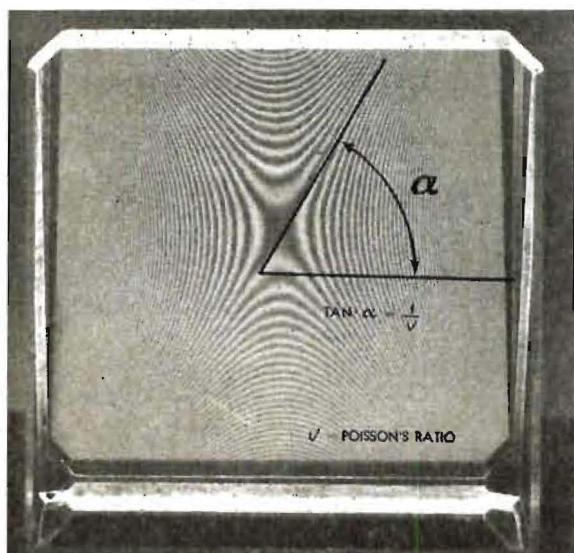
material, this is very close to the value of 0.5 theoretically required for analysis assuming incompressibility.

The measurement of linearity of strain response to stress and the measurement of creep constants required the fabrication of special equipment. The creep behavior of a thermoplastic is very sensitive to temperature variation and mechanical vibration and, often, moisture content. An environmental control chamber was built for these tests (see Figure 7) which provided temperature

Figure 7. **Environmental control chamber.**

control to $\pm 1°$ F, was isolated from sources of vibration, provided humidity control to ± 1 percent R.H., and which permitted visual observation of the discs during testing. The loading fixture inside the chamber provided several alternate loading configurations and used linear variable differential transformers for measurement of displacements up to one (1) inch with an accuracy of one-one thousandth (0.001) of an inch. Figure 8 shows the test apparatus with the environmental control chamber raised, the notations being as follows:

(1) P is point of application of load to disc and point of measurement of deflection.

(2) R is the reaction.

(3) Lever connects P to transformer core.

(4) L.V.D.T. is a 500 SL Shaevitz linear variable

Figure 6. **Measurement of Poisson's Ratio by pure bending of plate.**

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differential transformer whose primary is excited by a 6-volt power source.

(5) Load is applied at transformer core.

(6) V.T.V.M., the vacuum tube voltmeter, measured the secondary voltage of the L.V.D.T. through the switch box providing deflection data.

The first experiment conducted was for the purpose of measuring the linearity of strain response to stress in a loading configuration conforming to that of a disc being stored in an off vertical position. Because warp must be of a larger order of magnitude to affect playback, it was necessary to use relatively large loads to produce the required deflections. Figure 9 summarizes the results of this test. The discs were simply supported in the horizontal position by two diametrically opposite hemispherical supports at the disc edge (R_a and R_b). The discs were loaded at the edge and at 90° to the supports with two simply supported weights connected to the cores of the L.V.D.T.'s which measured displacement at this point (P_c and P_d). The displacements of the loaded points were measured as a function of time for 100 hours at 80° F and 50 percent R.H. These displacements were

Figure 8. Deflection measurement system of creep test apparatus.

NOTE: L.V.D.T. for P_3 failed during test

Sym-bol	Cold Flow
$P_1 = 0.231^l$	O 0.076
$P_2 = 0.385^l$	□ 0.170
$P_4 = 0.713^l$	△ 0.332
$P_5 = 0.883^l$	◇ 0.389

Vinyl Compound "A"
12" Blank Discs   0.034" Thick
Temp. 80°F.   R.H. 50%

Loading Diagram

$P_c = P_d = R_a = R_b$

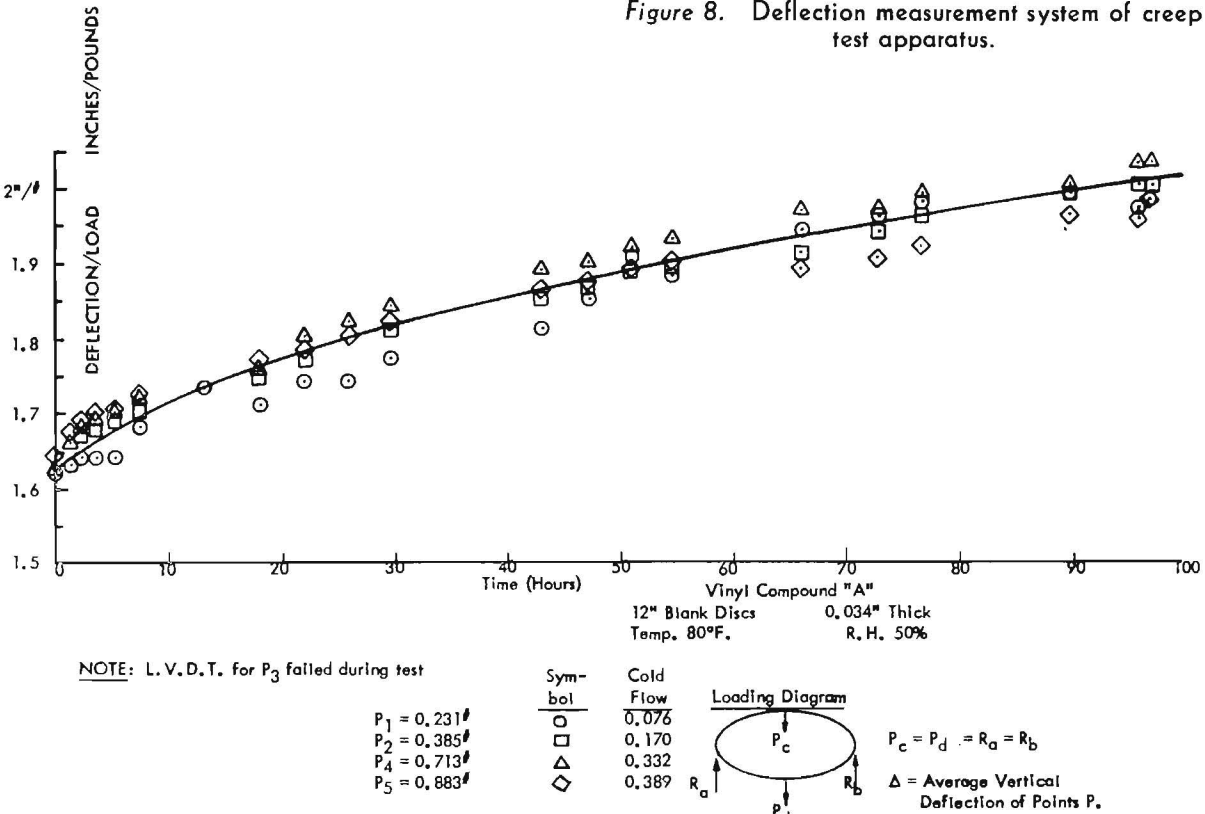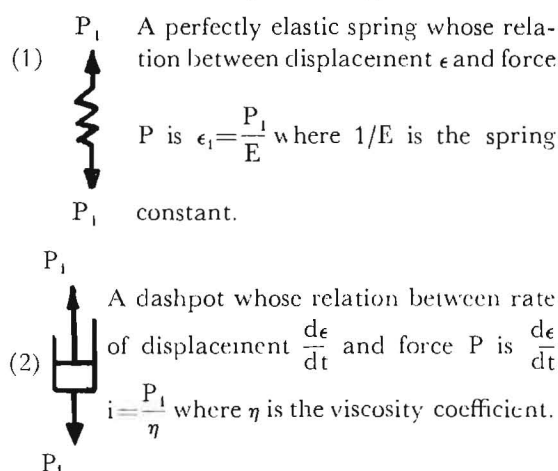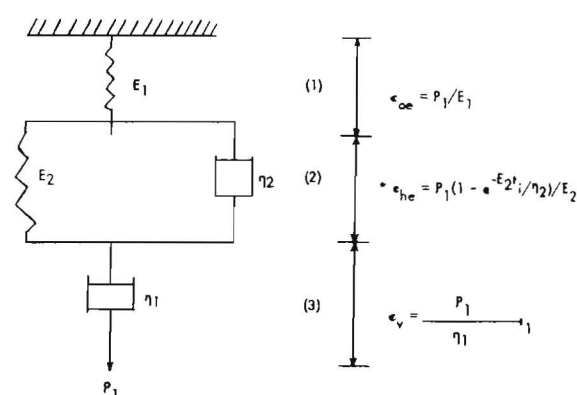△ = Average Vertical Deflection of Points P.

Figure 9. Stress superposition test.

divided by the value of the load and plotted as a function of time. At the end of the test, the disc warp was measured and recorded as cold flow. This experiment showed that disc formulation approaches the ideal linear viscoelastic material within the range investigated sufficiently well to permit the simplest method of analysis to be used. This method consists of constructing a mathematical model of the material which can best be visualized as a mechanical device as in Figure 10. (1) (11) (12)

This device is made up of two types of elements:

(1) P_1 A perfectly elastic spring whose relation between displacement ϵ and force P is $\epsilon_1 = \dfrac{P_1}{E}$ where 1/E is the spring P_1 constant.

(2) P_1 A dashpot whose relation between rate of displacement $\dfrac{d\epsilon}{dt}$ and force P is $\dfrac{d\epsilon}{dt}$ $i = \dfrac{P_1}{\eta}$ where η is the viscosity coefficient. P_1

These elements are combined into units which have a linear strain response to a load as indicated:

$$*P_1 = E\epsilon + \eta\epsilon$$

$$\epsilon = (e^{-Et/\eta})\left[\epsilon_0 + \frac{1}{\eta}\int_0^t Pe^{Et/\eta}dt\right]$$

if P = const., $\epsilon = \epsilon_0(e^{-Et/\eta}) + \dfrac{P}{E}(1 - e^{-Et/\eta})$

Figure 10. Model of PVC molecular forces.

This model is more than an abstraction; it depicts actual molecular behavior. If a constant load is applied to a PVC disc the following deformations will be observed:

(1) An immediate deformation called ordinary elastic or glass elastic deformation (E_{oe}). This is a storage of internal energy by bond stretching or valance angle deformation.

(2) A time dependent deformation called high elastic or retarded elastic deformation (E_{he}). This is a storage of internal energy by changes in molecular configurations. In this theory, the main assumption is that of a quasi-free rotation around single carbon—carbon bonds which results in a most probable coiled up form for the average chain molecule. An external force changes this shape, and, on the removal of this force, thermal action results in a gradual reattainment of the preferred configurations. This recovery happens in accordance with the statistical interpretation of the second law of thermodynamics and is not caused by forces as is ordinary elasticity.

(3) A time dependent deformation called flow (E_v). This represents energy dissipation by intermolecular Brownian movement of a translatory character or the movement of a molecule as a whole with respect to other molecules. It can also represent chemical stress relaxation.

When the load is removed, the following deformations will be observed:

(1) Immediate recovery of the glass elastic deformation.

(2) Time dependent recovery of the retarded elastic deformation.

(3) The viscous flow component will not be recovered and this permanent change in shape is called creep.

In order to approximate the behavior of a real material, it is necessary to couple many of these units together in parallel and the resulting equation for total deformation of a suddenly applied load that is thereafter kept constant becomes

E total = $n(E_{oe} + E_{he} + E_v)$ where n is the number of units. Fortunately, simple algebra reduces this equation to

$$E\ total = \frac{Pi}{Ei}[1 + f(t_1)] \quad (see\ Figure\ 10)$$

which is equivalent to

$$E\ total = \frac{Pi}{E_t}$$ where E_t is a time dependent modulus of deformation.

While the model has been developed for a simple

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direct stress and a simple loading history, the principle can be extended to any stress condition without loss of validity. The principle is simply the substitution of E_t, a time dependent modulus of elasticity, for the modulus of elasticity in the calculation of deformations using the formulae of the theory of elasticity. E_t is a very complicated function of both time and temperature but it can be obtained empirically.

If the time scale of the prediction is comparable to the time scale of the experiment, curve fitting techniques can be successfully used to provide formulae to approximate E_t. (1)(9)(16) A far more powerful tool, however, is the time-temperature superposition principle or method of reduced variables of Leaderman, Tobolsky and Andrews. (21)(22)(23) This principle assumes that the time function at one temperature is equal to the time function at another temperature times a constant and, hence, curves of E_t, or log E_t versus log t can be superposed by means of a horizontal shift along the log t axis. A matter curve applicable for all temperatures and all times, then, of E_t can be drawn by performing many short time tests at different temperatures and superposing the resulting curves. This has proven to be true for many linear viscoelastic polymers above the glass transition temperature and is the technique used for analysis in this study.

Short time tests of the discs showed that, supported and loaded as in the test for linear viscoelasticity, the deflection of the points at which the concentrated load was applied with respect to the supports obeyed the equation:

$$y = \frac{614,000}{E}\ P + \frac{16,600,000}{E}\ \rho$$

where y = deflection in inches

P = concentrated load in pounds

ρ = uniform load over disc surface in pounds

and E = modulus of elasticity in pounds/square inch.

As noted above, the substitution of E_t for E in this equation is all that is required to change the equation from an elastic equation which predicts deflection as a function of load to an equation which predicts deflection as a function of both load and time.

Using the same equipment as was used for testing linearity, a series of experiments were made to evaluate E_t. Three discs, loaded identically, were used in each test and the deflections were measured as a function of time (see Figure 11). Humidity was controlled at 50 percent R.H. and tests were run at constant temperature for 1000 hours. Tests above 110° F proved to be valueless because of interfering deformation from other sources. Figure 12 summarizes the results of this series of tests and Figure 13 is the master curve drawn by superposing the curves of Figure 12.

Using the values for E_t obtained empirically and modifying the empirical equation for deflection in the horizontal position by multiplying it by the sine of the angle between the disc axis and a vertical line, an estimate of the deformation of such a disc stored at 10° off vertical and at 80° F without being moved for 20 years was obtained (see Figure 14). As the master curve indicated that the same magnitude of deformation would occur if the disc were exposed, under the same conditions, to a temperature of 110° F for 1000 hours, three discs were placed in the chamber at 10° off vertical at 110° F for 1000 hours. The predicted deformation was attained in each case within satisfactory limits to indicate the validity of this approach.

These data *indicate that a plastic phonograph record can be stored in the vertical position for many decades without excessive warp due to creep caused by gravity loads if the following precautions are taken:*

(1) Maintain moderate temperature ($<80°$ F).

(2) Provide as near vertical attitude as is feasible.

(3) Prevent discs from loading other discs.

An investigation of the horizontal storage attitude indicated that the *high bearing stresses on the lands of the modulations caused surface imprint which impaired playback qualities.* At first glance, it might seem that the surfaces of discs stored in the horizontal position are uniformly loaded. Unfortunately, this is true only after the plastic surface has been deformed sufficiently to fit around the unevenness of these surfaces and the materials between them. If, for example, there are wrinkles in the storage package or dust grains between the discs, all of the load between discs must be transmitted through these line or point contacts until the wrinkles or dust grains are pressed deeply enough into the disc surface for other portions of the surfaces to come into contact. Figure 17 shows the impress of package wrinkles in a disc surface caused by loading the disc with three other discs at 110° F for 100 hours. Figure 18 shows the impress of corrugations of a cardboard separator which developed on the surface of a disc stored by the Library of Congress
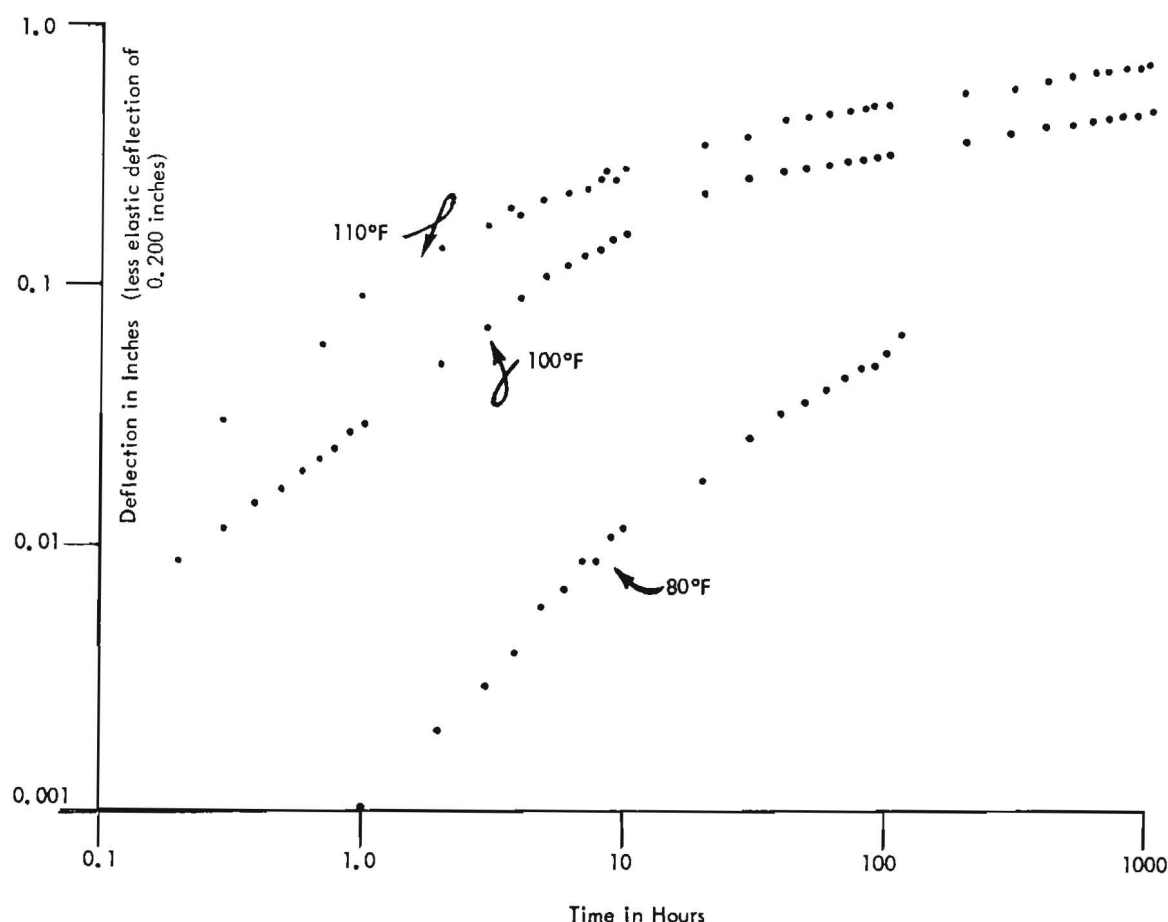
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Figure 11. Experimental deflection data for vinyl discs loaded as shown in figure 12.

(this disc was also badly warped by relaxation of microscopic stresses). This portion of the study forms the basis for the recommendation that plastic discs be stored in the vertical attitude.

Physical Deformation Induced by Residual Stress

The results of the creep tests help to justify the use of vertical storage attitude, but, as in the chemical degradation study, left unexplained the warped plastic discs found in library stacks. A study of the history of some of the deformed discs showed that such warp had developed in horizontal storage at moderate temperatures and that, of ten, the deformed shape was not compatible with deformation due to creep induced by gravity loads. This indicated that these deformations were the result of residual stresses introduced in the molding process.

In a thermoplastic there are two kinds of residual stresses (or strains) which can cause such dimensional changes. The two kinds of residual stresses (or strains) will be denoted as macroscopic and

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microscopic stresses, for the sake of convenience even though the nomenclature is not descriptive of the actual mechanisms involved.

Macroscopic residual stresses are real recoverable stresses and are of two kinds: reaction stresses and layer stresses. An excellent example of reaction stresses is provided by the shrink fitting of an iron tire on a wooden wagon wheel. It is evident that the tensile forces in the tire are balanced by compressive forces in the wooden wheel. These stresses can be evaluated by cutting out a spoke or cutting the tire and measuring the resulting dimensional changes. Layer stresses can exist in a disc as uniform biaxial compression in the surface layers and uniform biaxial tension in the core with the distribution of forces over the thickness having a zero resultant and zero moment. In this case, no deformation would be observed on cutting a section from the disc through the entire thickness but these stresses can be evaluated by removing successive layers from a surface of the section and measuring the resulting deformations. In both cases, ordinary

Time (Hours)
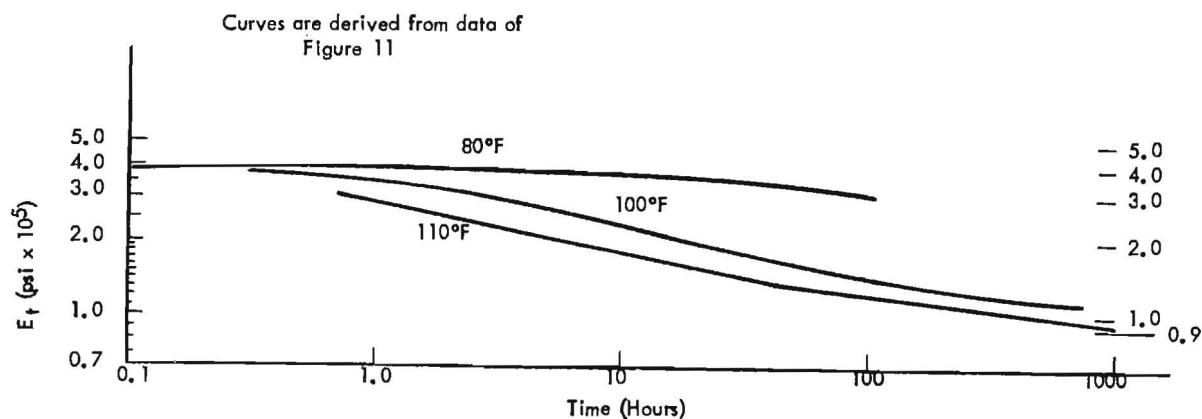
Sample Calculations:
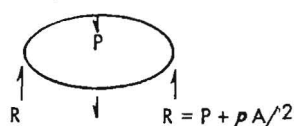
$P = 0.068^{\#}$ Disc is 1/20 inch thick
$p = 0.0029^{\#}/\square"$ y is deflection at P
$A = 113\ "$

$R = P + pA/2$

Loading Diagram

$E_t = 89,600 \div y$ Reduced Equation for $E_t = f\ (y)$
At 80°F, 100 Hours, $y = 0.287$ Experimental Result
$E\ (80°,\ 100\ hours) = 8.96 \times 10^4 \div 0.287 = 3.12 \times 10^5$ Derived Value

Figure 12. Graph of log E_t vs. log time.

Time (Hours) at 80°F

At 100°F |1 |10 |100 |1000 |10,000

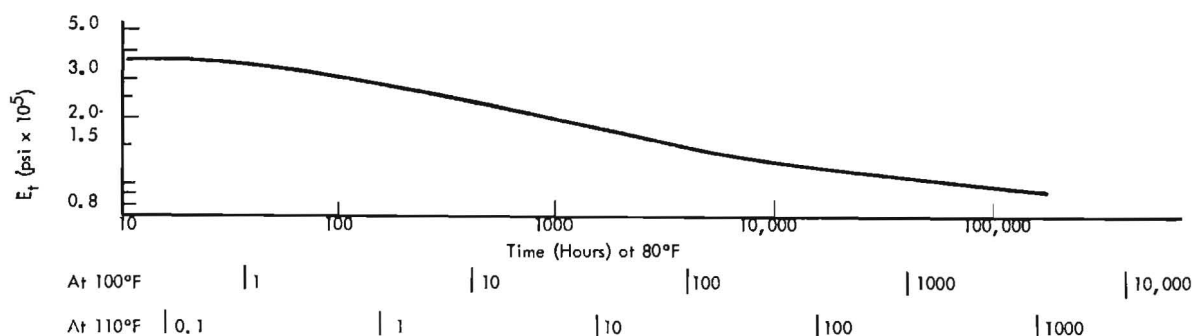At 110°F |0.1 |1 |10 |100 |1000

Figure 13. Master curve of log E_t vs. log time for 80° F. with time scales for 100° F. and 110° F. formed by superposing the curves of figure 12.

elasticity is involved and the deformations occur immediately.

In order to measure deformations from macroscopic residual stresses, a Whittemore strain gage with a two inch gage length accurate to 0.0002 inches was chosen to measure changes in length and a dial gage jig for measuring curvature of the type described by Welch and Quackenbos (24) was fabricated.

The specimens tested were new unmodulated ungrooved discs, especially pressed by two different manufacturers, and five-year-old unwarped discs purchased on the open market. Two different

trepanning configurations were used for each type of disc. One configuration consisted of drilling eight concentric rings of two inch gage marks spaced ½ in. apart radially beginning with a ring ¼ in. from the edge of disc. These rings were cut from the disc on lines midway between the concentric rings of gage marks using a lathe. After cutting, the gage marks were measured, the rings were broken and the gage marks remeasured. There was no change in shape or dimension noted. The other configuration consisted of an array of Y-shaped gage mark rosettes which were formed into one set of new discs during pressing and
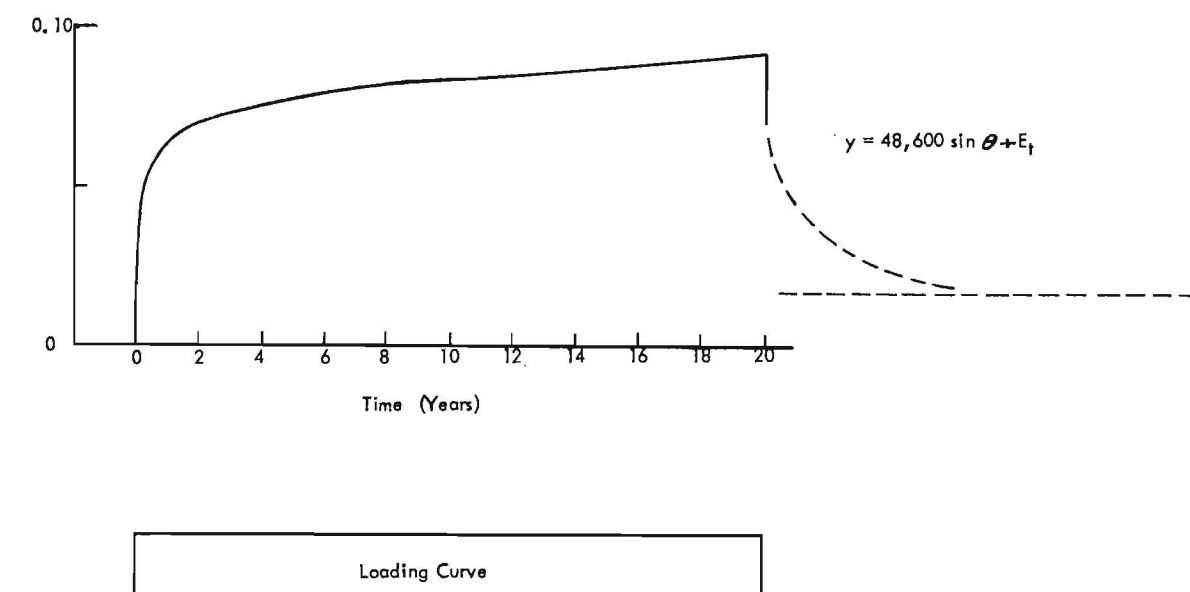
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Figure 14. Estimate of deformation of a vinyl disc stored at 10° to the vertical without being moved for 20 years at 80° F.

drilled into the other discs. Specimens including these rosettes were cut from the discs with a saw and measured. There was no change in shape or dimension noted. These results showed that no reaction stresses existed in the discs tested.

The same specimens which had been cut from the discs for reaction stress measurements were used for the investigation of layer stresses. Layers were removed from one surface of each specimen by either milling or solvent etching. In no case were there the dimensional changes which indicate layer stresses. A sufficient number of tests were made to demonstrate that *there were no macroscopic residual stresses of intensity great enough to warp the discs used for test articles.*

Microscopic residual stresses are not real recoverable stresses, but can cause strains or deformations just as do the macroscopic residual stresses. While the mechanism involved in macroscopic residual stresses is that of ordinary elasticity, the mechanism involved in microscopic residual stresses is that of high elasticity. This mechanism is termed the molecular configurational strain. (1) (11) (12) In an assemblage of linear molecules, there will be a statistically preferred (or most probable) molecular configuration; this "average" molecule, separated from its neighbors, might be depicted as:

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(a) *Statistically Preferred Molecular Configuration*—If the average molecular configuration is changed by external forces, and the forces then removed, the random Brownian movements will attempt to restore the system to the statistically preferred configuration. This process will be hindered by the barriers set up by neighboring molecules. If a molecule such as is depicted in (a) is subjected to a stress, F, an extreme result could be depicted as a completely oriented system of elongated molecular segments.

(b) *Completely Oriented System of Elongated Molecules* where the intermolecular barriers are too great to permit a molecule to relax to the entangled, curled system. An increase in temperature increases the Brownian movement and reduces the energy required to surmount a barrier so that there would be a temperature for any discrete barrier level above which a molecule of (b) would revert towards the preferred configuration (a) if the external force which created (b) is no longer effective.

As was previously noted, high elasticity strains do not occur nor are they recovered immediately, but are time dependent. From the theory of such strains, elevation of temperature results in a decrease in time required for such strains to occur as

well as the occurrence of strains which might not occur at far lower temperatures because the activation energy required for the relaxation of some molecular configurational strains can be higher than is attainable at the far lower temperatures. The study of the deformations which occur on elevation of temperature is not, therefore, an exact measure of the deformations which would normally occur at ambient storage temperatures, but it does furnish evidence as to the existence of microscopic residual stresses which can cause such deformations.

A group of discs was selected whose history and origin were identical with those used for the study of macroscopic residual stresses. These discs were marked and sectioned as before. The specimens and phonograph records were then placed in the environmental control chamber and observed as the temperature was slowly elevated. Both phonograph records and specimens warped and shrank. The deformations which occurred were similar to and of the same order of magnitude as those observed in discs which had warped in storage. The deformations observed were, in all cases, the result of shrinking caused by the recovery of molecular configurational strains with the warping being caused by differential shrinkage of different sections or sides of the specimens or phonograph records.

A differential thermal expansion apparatus of the type described by Dannis (5) was assembled to further explore this shrinkage. With this apparatus, a large number of tests were made of the shrinkage which occurred in specimens excised from records of different formulation and different origin. The results were quite conclusive as to the significance of the microscopic residual stresses in all the discs tested (including discs several years old). In nearly all cases, the amount of shrinkage increased from the center of the disc outward toward the edge. In many cases, it was greater on one surface than on the other. In magnitude, linear shrinkage was of the order of 0.1% to 0.2% which does not affect fidelity but is sufficient to cause warping (see Fig. 16).

The demonstration that serious warp and deformation can, and probably frequently does, result from the relaxation of microscopic residual stresses caused by molding is disheartening from the standpoint of long time storage of plastic discs. First of all, the warped surface is not developable so that the disc can not be satisfactorily flattened by the use of heat and pressure (see Fig. 15). Secondly, these stresses cannot be relieved by annealing without serious dimensional changes as macroscopic residual stresses can often be, because they are not elastic stresses in static equilibrium. The only way to prevent such warp is to improve the molding process and the only way to inhibit it is to reduce the storage temperature. Fortunately the amount of shrinkage which occurs is so small that it does not cause an appreciable frequency shift (the maximum measured value was a shift from the 10,000 cycle note of a new disc to 10,060 cycles after aging at elevated temperature) even if the disc is badly warped. The recording is

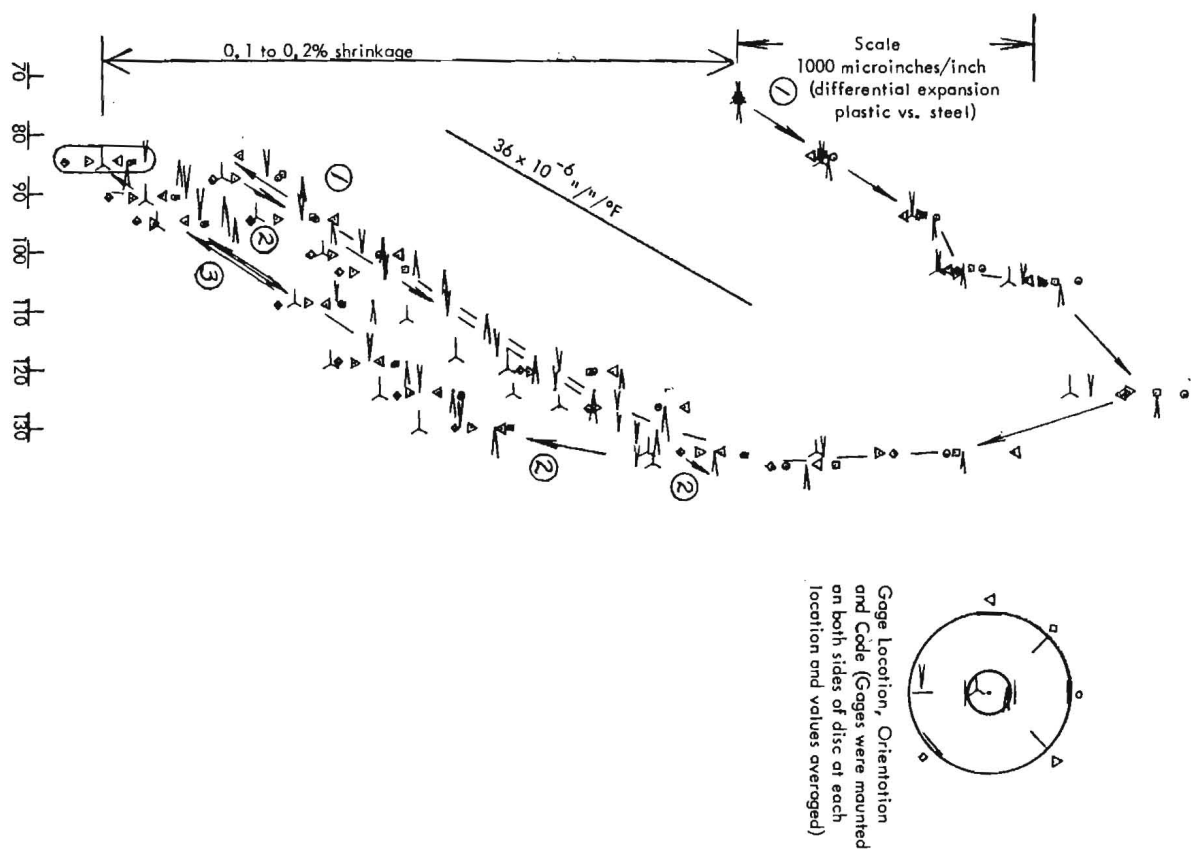*Figure 15.* Photograph of fluted edge warp caused by relaxation of microscopic stress.

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Figure 16. A strain gage survey of the relaxation of molecular configurational strains in a vinyl disc.
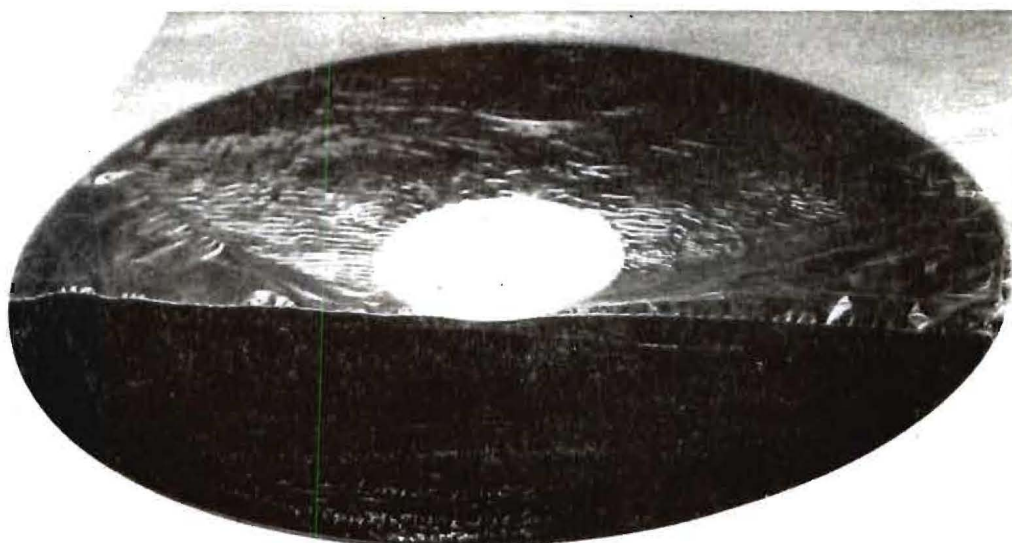

Figure 17. Surface imprint due to wrinkled polyethylene jacket and accelerated aging.
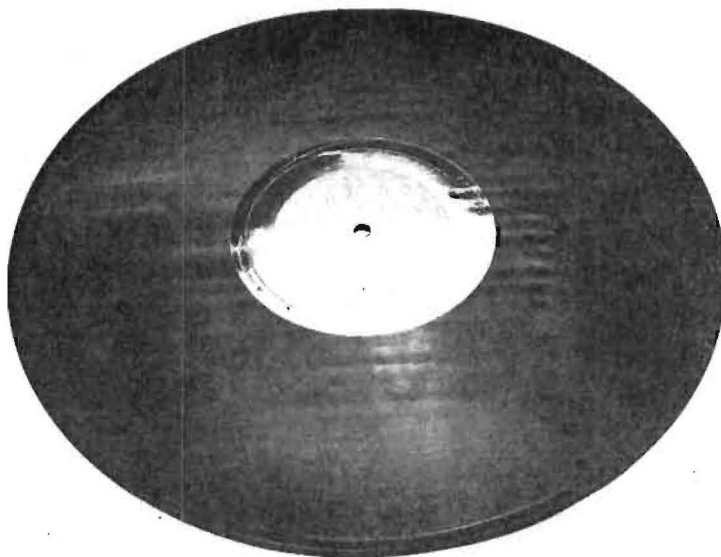
Figure 18. Surface imprint found on Library of Congress shelves.
(Horizontal Storage Attitude)

not necessarily lost if it is too warped for playback with conventional equipment. It would seem that a special pickup arm which will track on a badly warped phonograph record would prevent much of this kind of loss of valued recordings on plastic discs by permitting re-recording. A pickup arm which accomplishes this for 45 RPM discs is used in some of the coin operated phonographs (jukeboxes).

Physical Deformation Associated with Thermal Cycling and Humidity

Another cause of warping which is distinct from, but probably influenced by, microscopic residual stresses is thermal cycling. Plastics have very large coefficients of expansion, are poor conductors of heat, and the boundary conditions on the two disc surfaces are often quite different. The boundary conditions of a horizontally stored disc can be particularly bad because they may result in both a thermal gradient across the thickness of the disc and different restraints against expansion of the two surfaces. The result is that each cycle of temperature results in a small irreversible deformation, and these deformations are cumulative. Plastic discs and phonograph records were subjected to 24-hour cycles of temperature from 80° F to —40° F in both horizontal stacks and in the vertical attitude. The highest temperature used was below the temperature which had proved to cause warp within the test period by recovery of

molecular configurational strains of the particular discs or phonograph records tested. The top disc in horizontal stacks failed by warping in as few as five cycles while the discs maintained in vertical attitudes required fifteen or more cycles to failure. In both cases the deformed shape was conical and the discs could not be flattened.

Humidity cycling and exposure to high humidities proved to have no effect on the vinyl discs. This is to be expected from the low moisture adsorption of this material.

In summary, this portion of the study indicates that:

(1) Vinyl discs have an extremely long potential storage life with respect to chemical degradation if they are not exposed to direct sunlight or other sources of U.V. and are stored at moderate temperatures. This potential life is of the order of a century for well-made and properly stored discs. The chemical aging of these discs can be monitored by measuring the amount of effective stabilizer remaining in the disc (see p. 49).

(2) Vinyl discs can be stored in the vertical attitude for very long periods of time without appreciable warp being induced by gravity loads if the storage temperature is kept below 80° F and the discs are stored with care. However, suitable shelves to maintain vertical attitude would be required.

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(3) Serious warp is induced by both thermal cycling and the relaxation of microscopic residual stresses resulting from the molding process. Thermal cycling can be prevented in storage, but only control of the molding cycle can prevent the introduction of residual stresses. The relaxation of these stresses can be inhibited by use of low storage temperatures.

(4) Humidity control is not essential in the storage of vinyl discs except as a means of controlling fungal growth.

D. Surface Damage of Phonograph Discs Caused by Fungi and High Contact Stresses

Types of Surface Damage

The survey of the manifestations of degradation of stored discs indicated that surface damage (unrelated to mechanical damage caused by handling or playback) was a common result of storage. This surface damage consisted of surface imprint confined to the lands, etching of both lands and groove walls, and changes in surface texture of the lands. Surface damage appeared to be most pronounced in discs stored in the horizontal position but was not confined to such discs. Surface imprint was most noticeable in discs whose surfaces had been in contact with corrugated cardboard, but was also evident in discs protected by Kraft paper and polyethylene envelopes. Figures 17 and 18 show two cases of this kind of damage.

The manifestations could be caused by a number of agents, depending on the materials involved. Possible mechanisms are:

(1) Permanent deformation of the material due to high contact stresses between disc and packaging material irregularities.

(2) Chemical action of an ingredient of the packaging material on the disc material.

(3) The wicking action of a porous material with respect to a liquid or volatile plasticizer.

(4) Fungal etching of the disc material by fungi growing on the packaging material.

(5) Migration of a constituent of the packaging material into the disc material.

While not discounting the other mechanisms as potentially feasible, it was only possible to duplicate the surface imprint in the laboratory by fungal action and by deformation of the material due to gravity loads.

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Laboratory Investigation of Fungal Action—Discs

The Library of Congress was the source of most of these specimens and, because the climate of Washington, D.C., is peculiarly suitable for fungal attack of organic materials (92), the ability of fungi to cause such damage was investigated.

The discs inspected were classified into three categories:

(1) Discs on which fungi spores and mycelia were found associated with visible surface damage.

(2) Discs with visible damage which could have been caused by fungi growing on the disc, but without direct evidence of fungal activity. It was thought that fungi could have caused the damage under proper environmental conditions prior to removal upon subsequent cleaning.

(3) Discs with surface etching which could have been caused by the excretions of fungi growing not on the discs but on jackets or separators in contact with the discs.

This classification was somewhat arbitrary but was made to serve as a starting point in the investigation. In these categories were the following specimens:

(a) A laminate with cardboard core and shellac coating (1) and (3)

(b) An acetate disc with glass core (2)

(c) A shellac type disc (2) and (3)

(d) A vinyl disc (3)

These discs, together with new acetate, vinyl, shellac, and shellac type discs were placed in the chemical exposure chamber (Fig. 19). Corrugated cardboard which had been inoculated with soil and fungus spores was placed on the discs. The air in the exposure chamber was kept at 70° F to 80° F, saturated with moisture, and continuously regenerated. A luxuriant growth of fungi soon appeared on the cardboard and gradually spread to the discs.

After four weeks exposure, the discs were removed for inspection. Species identified were penicillia, aspergilli, mucor, and rhizapus. The most luxuriant growth was found along the lines of corrugation in contact with the discs followed, in descending order, by cardboard surface, acetate disc surface, shellac discs (containing natural waxes), shellac type discs containing resins derived from wood and sugar cane, and filled vinyl discs. Unfilled vinyl discs were etched by fungi growing on adjacent
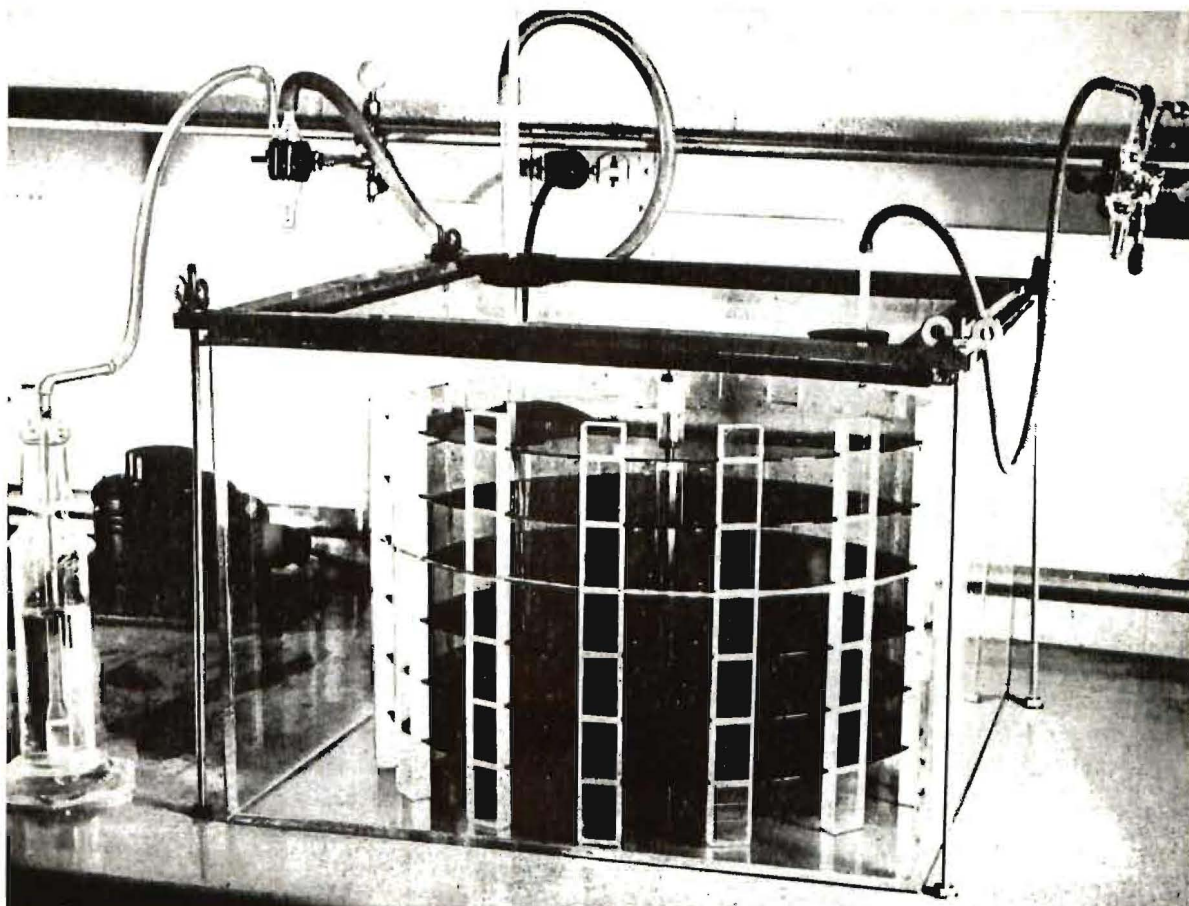
Figure 19.   Chemical exposure chamber.

materials and fingerprints, but did not seem to support growth itself.

Fungus mycelia could be seen plainly on the surface of the infected discs with the aid of a hand lens and a stereoscopic microscope. It was also noted that the mycelium grew down, into the grooves, indicating that it was growing on the surface of the discs and not on the separator. Smooth portions of records covered with fungi were further examined under a microscope. While observing the field, it was swept clean with a camel hair brush, in order to determine if any markings could be noted underneath the mycelium. It was easy to distinguish etchings made by fungus hyphae from ordinary scratches. The ordinary scratches were in straight or curved lines. Etchings made by hyphae were irregular and appeared to be more superficial. A vinyl disc, containing limestone and carbon black filler (a compound normally considered fungi resistant), showed both fungal growth and etching. Scratches on the surface of this disc,

known to cause noise in playback, were of the same order of magnitude as the fungal etching. This etching was most serious where fungal growth was most abundant, i.e., where the line of corrugations of the cardboard was in contact with the discs.

The results of this four weeks exposure appeared to confirm the suspicion that fungi were potential severe agents of disc deterioration. Accordingly, it was decided to expose disc materials to fungal activity for a six month period in order to obtain more information about this degradative agent.

Disc specimens were cut or broken into rectangles 2 inches by 3 inches in size. These rectangles were inoculated with common airborne or soil fungi: namely, aspergillus niger, aspergillus flavus, aspergillus terreus, alternaria humicola, fusarium sp, penicillium sp, and rhizopus nigricans. After inoculation, they were stacked with corrugated cardboard separators and placed in moist chambers. The moist chambers were kept at ambient temperature (72° F to 88° F). Additional stacks

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were placed in a cold room whose temperature was 37° F to 40° F and humidity was 55% R.H. to 85% R.H.

Other materials which are currently used for fabricating disc jackets or envelopes or are proposed for such use were also studied; this included materials in which fungicides had been incorporated. The materials were inoculated with the same fungi as above and placed on fungi inoculated agar in Petri culture dishes which were kept at ambient temperatures. It should be remarked here that the effects of exposure to high humidity are not inseparable from the effects of fungal activity in either discs or jacket material, as both can cause deterioration of plastic and natural organic materials, and high humidity is essential to growth of these fungi.

After six months incubation, the disc specimens were examined by hand lens and microscope for signs of deterioriation and the following results obtained: *

(1) Unfilled, unextended microgroove vinylite compound, containing lead stearate, carbon black and a dye. Fungi grew profusely on label and branched out over the disc surface. After cleaning, little, if any, etching caused by fungi could be observed. No embrittlement or loss of flexibility was noted. This material seems to be resistant to deterioration induced by moisture or fungal activity. (Compound A)

(2) This material is the same as noted in (1) above with the omission of carbon black: It behaved exactly as did the previous specimen. As far as resistance to damage by high humidity and fungi, the unfilled, unextended microgroove vinylite compositions proved superior to the other formulations. (Compound B)

(3) Filled, extended microgroove vinylite compound which contains natural waxes and a resin obtained by the destructive distillation of wood as well as $CaCO_3$: Some etching was noted where two different specimens of this material were in surface contact. The compound did not appear to support fungal growth and the fungus appeared to have grown on some other substrate with the mycelia penetrating between the surfaces in contact. After

*See "Bakelite" Molding Technical Release No. 10 for formulation background information. (104)

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this aging, some areas of the specimen were quite brittle while the remaining sections retained most of their flexibility. It is not known whether this was occasioned by humidity, fungal attack, or both together. This is an inexpensive microgroove formulation with too high a noise level for quality $33\frac{1}{3}$ disc manufacture. The most common use of this type of formulation is believed to be in popular 45 RPM's. (Compound C)

(4) Filled, extended regular groove vinylite compound containing more $CaCO_3$ filler and less extender (which is also believed to be superior in aging qualities to that of the previous specimen). Fungi appeared to grow only on the label, but some etching was observed on the surface. The only embrittlement noted was at the disc rim which might have been caused by the increase or decrease in concentration of one of the constituents in this area during molding. (Compound D)

(5) Shellac type normal groove compound using synthetic resins and $CaCO_3$ filler. This disc was seriously deteriorated by exposure to high humidity and fungi. Fungal etching was prominent over the entire surface. This disc was very brittle after exposure, probably caused by loss of plasticizer or one of the resins. (Compound E)

(6) Acetate, 1944 composition (nitrocellulose plasticized with raw castor oil). Specimens kept in cold room showed a slight fungus growth but no visible evidence of damage. Specimens kept at ambient temperature showed considerable fungus growth which produced little etching but complete loss of adhesion between core and coating. This loss of adhesion began at discrete points (making "blisters"), and spread to cover the entire area. The surface, though covered with spores and mycelia, was yet relatively clean and smooth. This behavior was identical with that observed when acetate discs were exposed to high humidity environments in stagnant air at elevated temperatures and indicates that loss of the plasticizer by fungal consumption and moisture extraction is responsible for this manifestation of deterioration.

(7) Acetate, new (nitrocellulose plasticized with modified castor oil and with added stable resins). This specimen proved far more resistant to high humidity and fungal deterioration than the previous specimen. No growth was noted in the cold room specimen, and the ambient temperature specimen was etched considerably only where it was in contact with cardboard. The same type of loss of adhesion between core and coating had begun, but had not progressed to the extent noted in the previous specimen.

Laboratory Investigation of Fungal Action—Jacket Material

The following results were obtained from the six months exposure of jacket material:
(1) Kraft paper was quickly disintegrated by fungal attack. This paper was cut from commercial disc jackets.
(2) Kraft paper impregnated with a commercial fungicide (which had an obnoxious odor) designed for such use did not disintegrate as quickly but the fungicide was beginning to lose its effectiveness by the end of the test period.
(3) Glassine was attacked and deteriorated as rapidly as the untreated Kraft paper. This glassine was cut from a commercial disc jacket.
(4) Polyethylene film was not seriously attacked by the fungi. Although some fungi were growing on its surface, they appeared to obtain no food from the polyethylene but, probably, from a lubricant used in processing the film.
(5) Nylon film behaved as did the polyethylene.

That some of the airborne soil fungi are able to utilize some of the organic plasticizers used in resin formulations as a source of organic nutrients is well recognized.

In this utilization the fungi in some manner dissolve out the plasticizers and thus reduce the tensile strength, and cause plasticized plastics to crack. Berk, Ebert and Teitell (26), in their investigation on the utilization of plasticizers and related organic compounds by fungi state that the diesters of saturated, aliphatic dibasic acids can be utilized by fungi, if they contain 12 or more carbon atoms. The maliates are fairly fungus resistant and the alkyl derivatives of phosphoric and phthalic acids do not serve as a carbon source for fungi.

Also an ether linkage into the carbon chain decreases its ability to support fungus growth. These investigators tested the ability of 24 common fungi to utilize 127 plasticizers and related organic compounds as a carbon source. According to Zobell (32, 33) it is a general observation that the susceptibility of hydrocarbons to oxidation by microorganisms increases with chain length up to 15 or 20 carbon atoms. Ethylene glycol is considered toxic to fungi but appreciable growth may be obtained at concentrations of 2% by weight. While the average ability of fungi to utilize a particular plastic as a carbon source may be low, yet it may be very susceptible to attack by a few microorganisms.

Recommendations to Minimize Fungal Action

This investigation indicates that in order to store records for a long period of time, it will be necessary to take several precautions in order to protect them from deterioration by fungi and moisture, and these are as follows:
(1) Use only those discs made of materials not readily attacked by fungi.
(2) Use special jackets not readily attacked by fungi. This excludes the use of common cellulosic materials for jackets and corrugated cardboard for separators unless these materials are protected from attack.
(3) Temperature and humidity should be carefully controlled. Relative humidity should be 55% or less. (92)
(4) The labels on the records should be made out of a fungus resistant material instead of paper.
(5) Adhesive for labels should be of a fungus resistant material such as polyethylene.
(6) Compatible fungicides are available for incorporation in *specific* materials but a general purpose fungicide suitable for incorporation in packaging material which will furnish long-time protection for phonograph discs without accelerating possible degradative reactions is, at present, unknown. (This conclusion was arrived at by a survey of commercially available fungicides and not by laboratory study; see preceding chapter.)

Surface Imprint Resulting from High Contact Stress

The other type of surface damage reproduced in the laboratory was surface imprint, which resulted from local yielding of the material under high con-

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tact stresses. For long-time loading, the actual value of a stress which will cause such yielding of thermoplastics is not of the magnitude which would be considered a high stress for a load of limited duration. The combination of a grooved disc surface with the irregular pattern of a warped cardboard or wrinkled jacket material results in a quite small bearing area which, given the proper combinations of temperature and load, will result in surface imprint. This imprint can result in poor playback because the deformed material may interfere with stylus tracking. Cellulosic materials are the worst offenders because of the dimensional changes induced by changes in moisture content. In packaging discs for storage, if surface imprint is to be avoided, it is essential to:

(1) Keep disc temperature below 80° F.
(2) Do not use materials with irregular surfaces, or which can develop irregular surfaces from humidity of temperature changes, in contact with discs.
(3) Do not store discs horizontally or with pressure exerted against their surface.

Section E following discusses recommended storage practices which include attitude and packaging.

E. Summary of Conclusions and Recommendations for Storage of Phonograph Discs

The major portion of this investigation was devoted to the study of phonograph discs. This may seem paradoxical to those who feel that magnetic tape has supplanted the phonograph record for instantaneous recordings so rapidly that the latter sound recording medium is already obsolescent for this purpose. Even if this were true, the fact remains that the present concern of the librarian is to preserve those sound recordings which he is now storing and to select the best sound recording medium for future acquisitions. Also, surprising as it may at first seem, published information on the deterioration of phonograph records is far more incomplete than the information that is available on magnetic tape. This is probably because the modern phonograph record was evolved over a long period of time by the gradual introduction of new materials and new techniques as they were developed by (or to meet the demands of) other fields such as plastics technology and electronics. Magnetic tape, on the other hand, was introduced in a technological period when not only were the ma-

terials and techniques available to take full advantage of its potentialities, but the method of design and development by scientific research had already been adopted by industry. Both of these sound recording media can be, and probably will be, improved and a major area of improvement is in that of potential storage life. At the present time, one advantage of the phonograph disc over magnetic tape is a sure confidence in the fact that certain types of discs can be safely stored for many decades while such longevity for tape is only a matter of surmise and conjecture. (67) There is no substitute for actual storage experience, and phonograph discs have a good head start in this regard.

Phonograph discs have been made and stored for over fifty years. So many early examples exist of each different kind of disc which are still in excellent condition that it is certain that the potential storage life of each type is at least equal to, and probably far exceeds, the length of time that each kind of disc has been manufactured. At the same time, there have been a sufficient number of discs that have failed to cause concern over the possible loss of valuable recordings. Undoubtedly, inferior materials, poor manufacture, and exposure to abnormal environments have played a part in many of these failures but it also seems evident that the use of proper storage facilities and techniques will inhibit storage deterioration and result in the attainment of maximum disc life.

In the previous sections, the mechanisms and manifestations of degradation of different types of phonograph discs have been discussed. It was noted that the response to the various environmental factors varied for the different types of discs and this poses the first question in defining an optimum storage environment; that is, should the types of discs be segregated in storage and stored in separate environments designed for the idiosyncrasies of the individual types or should a compromise storage environment be designed for phonograph discs as a group? The answer probably lies in the fact that library storage is not dead storage and that library storage facilities must, in themselves, be a compromise based on the parameters of space, economics, record availability, and record stability, and these demands seem to recommend the latter course of action.

Table 6 is a summary of the significant characteristics of the most common types of discs generally found in library collections.

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TABLE 6.—A SUMMARY OF THE AGING OF PHONOGRAPH DISCS

A. COMMON TYPES OF DISCS

Nomenclature	Acetate	Shellac	Vinyl
Basic Formulation...........	Nitrocellulose (plasticized with castor oil) coating on metal core.	*Shellac, copal resin, mineral filler.	Copolymer of vinyl chloride-acetate, unplasticized.

B. THE EFFECT OF ENVIRONMENTAL FACTORS

	Acetate	Shellac	Vinyl
Fungi Rating..............	Very susceptible..........	Often very susceptible; depends on formulation.	Resistant to growth; not resistant to etching.
Reaction to Excess Moisture..	Plasticizer loss; chemical degradation; some dimensional changes.	Chemical degradation; serious dimensional changes.	Unaffected.
Heat Resistance:			
a. High Temperature.....	Poor....................	Poor....................	Poor.
b. Thermal Cycling......	Probably accelerates loss of coating adhesion.	Not detrimental to a good genuine shellac but warp inducing in shellac types.	Very detrimental dimensionally, inducing warp.
Light Resistance...........	Very poor................	Good to poor............	Poor.
Imprint and Abrasion Resistance.	Poor....................	Poor....................	Poor.
Resistance to Attack by Oxygen and Atmospheric Contaminants.	Poor....................	Poor to good............	Fair.

C. THE RESULTS OF AGING

	Acetate	Shellac	Vinyl
Probable Modes of Failure (in order of seriousness of results).	Catastrophic failure of coating; embrittlement.	Embrittlement; warping....	Warping; embrittlement.
Probable Causes of Failure....	Loss of plasticizer; denitration of polymer.	Loss of extender; condensation of shellac.	Internal stresses; loss of extender; cross-linking.
Disc Changes..............	Increase of noise with no significant change in signal.	Increase of tensile modulus of elasticity and loss of impact strength.	Warping.

*This is a best formulation, not necessarily a most common one. There is not a typical shellac formulation.

An optimum compromise storage environment for these discs which is compatible with library operations would:

(1) Prevent fungal damage by not providing an environment suitable for fungal activity. This can be accomplished by:

    (a) Reducing fungal nutrients to a minimum by keeping discs clean and not using nutrient packaging materials for storage.

    (b) Reducing moisture on disc surface below amount required by fungi.

(2) Keep moisture content of disc environment at a satisfactorily low value which is, at the same time, not so low as to cause undesirable changes in certain materials. A moisture content in equilibrium with 50% R.H. at 70° F seems to be satisfactory.

(3) Keep temperature reasonably constant and at as low a figure as is compatible with human activity.

(4) Deny access of ordinary sunlight or artificial lighting of the shorter wave lengths (such as certain mercury vapor fluorescent lights).

(5) Store all discs in the vertical attitude, keep them clean, do not use rough surfaced packaging materials, and do not permit

sliding contact of disc surface with other surfaces.

(6) Provide a vapor and gas barrier between the disc and the ambient atmosphere. Inert gas purging of the package prior to closure is feasible in a large operation, but is probably not necessary as just prevention of the renewal of oxygen and atmospheric contaminants in the disc environment should reduce the attack by the agents to a tolerable level.

The extent to which these measures can be taken is, of course, dependent on the operation of the individual library. If possible it is, of course, desirable to air-condition completely the entire library and keep its environment dust free, at 50 $\pm 10\%$ R.H. and $70 \pm 5°$ F. If this is not possible, the playback and packaging facility environments should meet these standards and the stacks should meet the temperature standards.

The technique of handling discs should be carefully supervised. Discs should be kept clean both for playback and storage. The techniques used in the laboratory for this study were tedious but effective. Routine cleaning was accomplished by using two commercially available systems:

(1) Prior to playback or packaging: a sparingly applied detergent solution with an applicator of sheared acetate velvet fibres.*

(2) During playback: a sparingly applied ethylene glycol solution with a brush and mohair applicator pad.**

Other systems of dust control and cleaning (such as spray on antistatic compounds, treated cloths, dampened synthetic sponge, and radioactive air ionization) were tried but did not prove as satisfactory as did these techniques. More drastic cleaning (called for in cases like the removal of gummy films from acetate discs) was accomplished by washing the disc in a lukewarm detergent solution, rinsing with distilled water from a wash bottle, quick drying in warm air from a hair dryer, and conditioning the disc in the 70° F, 50% R.H. environment. This drastic cleaning was, of course, only performed when necessary. The disc grooved surfaces were never handled with bare hands (rubber gloves being used) and the discs were inserted into and removed from their packages without touching the grooved surfaces or permitting sliding contact between packaging material and grooved surface.

*Lektrostat Record Cleaning Kit, Dexter Chemical Corp.
**ESL Dust Bug.

The present commercial packaging materials used in disc storage are all unsatisfactory in one regard or another. A specially designed package is recommended which:

(1) Is itself protected from the agents of degradation so that it will not warp, grow fungi, or otherwise aid in disc degradation.

(2) Will provide a gas and vapor barrier between the disc and the ambient stack atmosphere.

(3) Will present a smooth surface to the disc and will permit disc insertion and withdrawal without sliding contact between disc and package.

(4) Will be stiff and have some structural strength to help vinyl and shellac disc resist warping and so that it will not itself deform so as to cause surface damage to disc by high contact stresses.

There presently exist a number of satisfactory packaging materials and, with the rapid developments in the packaging industry, there will probably be superior materials to these in the near future.

At the present time, the most satisfactory material seems to be a laminate of polyethylene/paperboard/foil/polyethylene. The paperboard furnishes the necessary stiffness to support the polyethylene and aluminum films and prevent dimensional change or wrinkling of these materials as well as to aid the vinyl and shellac discs in resisting warping. The aluminum foil is an effective vapor barrier to deny access to oxygen and deleterious atmospheric contaminants. The polyethylene furnishes a smooth, fungi resistant surface and also is a moisture barrier for both the paperboard and the discs. Recommended specifications for this laminate are:

(1) Paperboard—34 point bending chip grade boxboard (0.034 inch caliper).

(2) Foil—Dead soft aluminum foil (military specification MIL–A–148A) of 0.001 inches thickness.

(3) Polyethylene—developments in this field are being made so rapidly that no suitable specifications for the latest and best polyethylene coatings are available. Within the past year, the introduction of glueable polyethylene film, medium high density polyethylene, and very thin films have made obsolete the polyethylene modified paraffin wax coating which would have been recommended but a few months ago. Probably the best current practice would

be to use an 8 lb* conventional low-density polyethylene** extrusion coating on the foil and a 15 lb conventional low-density polyethylene coating on the paperboard and to laminate the coated foil to the coated paperboard with polyethylene; both techniques and materials should soon be supplanted by superior and more economical coatings.

It is difficult to estimate the costs for this material with no knowledge of the production volume required. However, recent price information indicates that, for 12 in. discs, the following cost data are approximately correct.

Kraft paper sleeves...............	$0.01
Polyethylene film sleeves...........	$0.02 to $0.05
Boxboard envelope...............	$0.06 to $0.09
Proposed package...............	$0.15 to $0.20

Figure 20 outlines two feasible package designs.

Prior to insertion of the disc into an envelope, the disc should be clean, and both disc and envelope should be in equilibrium with an atmosphere of 50% R.H. and 70° F. A conditioning (or packaging) room is recommended for this operation. When a disc is received, or if it has been exposed to other than the optimum environment, it should be conditioned for 24 hours before packaging. Even if it is not feasible to aircondition the entire library, it is recommended that the playback facilities and conditioning room have the recommended environment and be dust free. Packaging of a disc with a moisture content higher than recommended may result in a detrimentally high humidity inside the package.

After packaging, the discs should be stored in the vertical attitude without pressure on the disc surface or the opportunity for off vertical attitude.

*Weight, in lbs/3,000 sq ft (reams). 8 lb=0.5 mil thick
15 lb=1.0 mil thick

**Petrothene 205 or equal.

This can be accomplished in at least two ways. One system is to use a compartmented shelf, with each compartment limited in size to accommodate from but one to two dozen packaged discs. A compartment which contains discs should be kept full of either packaged discs or packaged discs and fillers so that packaged discs are kept upright but not so that force is required to remove or insert a disc. Another system is to use shelves whose interior height is but very little greater than the package dimension, with well aligned slotted metal strips on both top and bottom of the shelves so that each packaged disc is supported in the vertical attitude independently of other discs. Figure 21 depicts these systems.

There are two other packaging techniques, presently used by the foods industry, whose potential value should not be neglected. One of these techniques, which could be *applicable to large collections of precious but very seldom used discs*, is inert gas packaging and the other is the aluminum foil-laminated corrugated box for temperature control during shipment of sound recordings. The application of these techniques to sound record preservation would be a worthwhile endeavor for industrial development and use.

Recordings should be re-recorded when necessary to insure preservation. At present, no completely satisfactory method is available to tell when this needs to be accomplished. As discussed previously, physical inspection for warping, fungus attack, or other visible evidence of deterioration is useful and should be done periodically. Also, there is evidence that detectable changes in the chemical composition of the record can be used to indicate incipient failure due to chemical deterioration, although more information is needed to develop analytical techniques and surveillance procedures. This aspect of the problem might be made the subject of additional study.
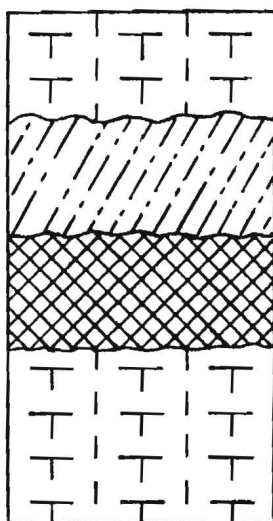
Proposed
Package
Designs
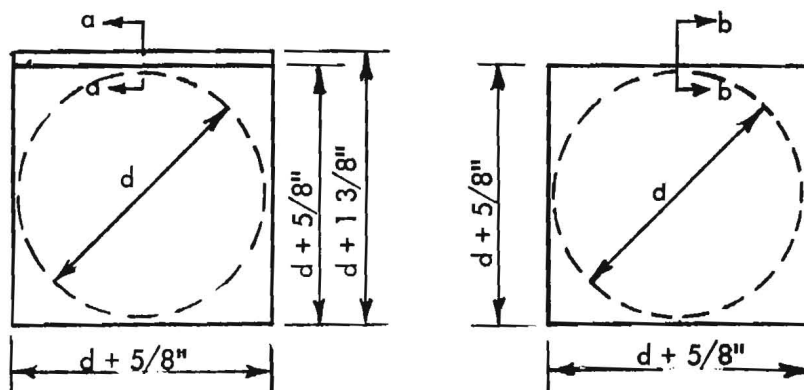
d = disc diameter
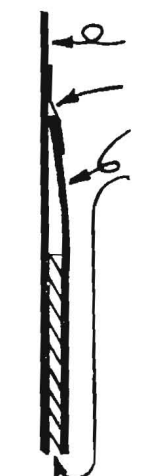
PACKAGING MATERIAL
PRESSURE SENSITIVE TAPE CLOSURE
PACKAGING MATERIAL

DISC

Polyethylene

Cardboard
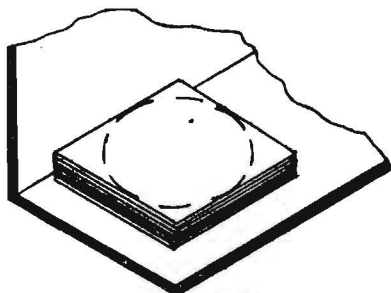
Aluminum Foil
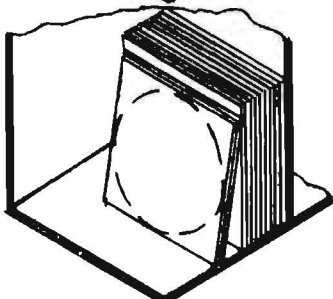
Polyethylene

Section a-a

Section b-b

NOT TO SCALE

Packaging Material
(See Text for Material Thickness)

*Figure 20.   Proposed disc storage packages.*

Horizontal Stacking – Poor; causes
surface imprint in all discs and warp
in plastic and shellac discs because
of different boundary conditions of
restraint and temperature on different
sides.

Off Vertical Stacking – Poor; causes
both surface imprint in all discs and
warp of plastic and shellac discs from
poor boundary conditions and gravity
loads.
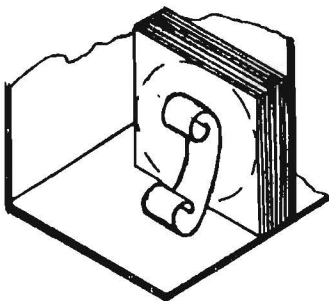
Spring Loaded Vertical Stacking – Poor;
causes surface imprint, poor boundary
conditions.
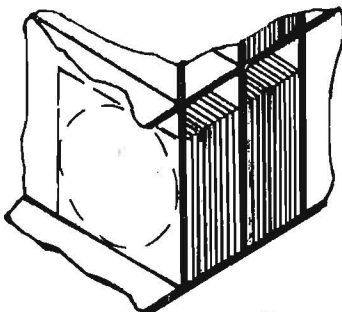
Full Compartment Vertical Stacking – Good;
recommended maximum 20 disc/compartment
Compartments in use should be kept full of
discs or discs and fillers.
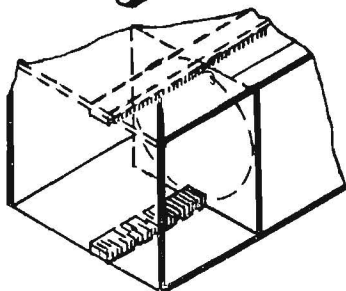
Template Controlled Vertical Stacking –
Good; slotted template can be made of
metal with very thin "fins". Slots
should be well aligned vertically and
bottoms of slot should be at or below
shelf level.

Figure 21. Very long time disc storage practice and shelf design.

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IV. THE STUDY OF MAGNETIC TAPE

A. Outline of Experimental Work

Magnetic tape was introduced into this country shortly after World War II. By 1950, it had been developed into such an excellent product that it has virtually replaced acetate discs as an instantaneous recording medium, and it is making some inroads into the duplicated recording field heretofore dominated by the plastic disc.

The experimental work performed on tape by the Institute largely duplicated portions of previously reported investigations by others. These studies consisted of:

(1) Investigations of the dimensional stability of the base as it is affected by:
    (a) Variations in winding tension
    (b) Variations in humidity
    (c) Variations in temperature
    (d) Reel design and poor winding
    (e) Variations in thickness and kind of base material

(2) Investigations of the stability of the coating as it is affected by:
    (a) Winding tension
    (b) Base material
    (c) Temperature
    (d) Humidity

(3) Investigations of the changes in magnetization induced by:
    (a) Temperature
    (b) A.C. Fields
    (c) Time
    (d) D.C. Fields

and represent many years of work by the original investigators. The work performed on this project by the Institute served primarily as confirmation of conclusions previously arrived at or, in some cases, to reconcile differences between the conclusions of previous investigators.

The tapes which were tested consisted of new samples of all of the different kinds of tapes presently manufactured by the four major tape manufacturers of this country together with some samples of older tapes. The Library of Congress recorded frequency tapes single track at 15 inches per second (level α—12 DBM across a 600 ohm non-inductive resistor) at 25, 50, 100, 200, 400 cps and 1, 2.5, 5, 10, 12, 15 kc and tone burst tapes single track, 15 ips, (level α—4 DBM across a 600 ohm non-inductive resistor) at 400 cps, 1000 cps, 5kc and 10 kc. Blank tapes and constant frequency tapes were also used in the tests.

Playback and instrumentation equipment used was a professional type tape recorder, a frequency counter, a V.T.V.M., an oscilloscope, a variable band pass filter, and a speaker. A humidity chamber and an oven with humidity control were used to expose the tape to the following conditions:

    (1) 1000 hours exposure to 150° F and low humidity.
    (2) Twenty cycles of 12 hours at 150° F and low humidity and 12 hours at 75° F and 50% R.H.
    (3) Ten cycles of 24 hours at 100° F and 100% R.H. and 24 hours at 75° F and 50% R.H.
    (4) Exposure to A.C. fields for periods up to one month.

Control tapes were maintained at ambient (approximately 75° F and 50% R.H.). The test tapes included tapes wound under different tensions and with varying perfection of wind. Also, during exposure to cycles of humidity and temperature, some test tapes were rewound at each cycle while others remained undisturbed. Three types of reels were used—five inch plastic, seven inch plastic, and ten inch N.A.R.T.B. metal reels. It would, of course, have been desirable to use far longer exposure times and a greater variety of tests but this was not feasible in this investigation. Exploratory tests indicated that more rigorous conditions were not realistic. Despite the cursory nature of the laboratory investigation, there were noticeable and measurable changes in the backing, coating and magnetization of the tapes which, together with the comprehensive information available in the literature, justify the following remarks (see Bibliography, especially the articles

by Daniel and Axon, (47) Latham, (63) Radocy, (67) (69) Herr and von Behren, (56) Westmijze, (78) and the Sound Talk bulletins (82) which provide complete empirical graphs of the phenomena referred to).

B. Base Material

Kraft paper, Polyvinyl chloride, cellulose acetate and Mylar (polyester) film have all been used as a base material for tapes. This study was restricted to the superior cellulose acetate and Mylar base tapes because most American made tapes are of these types. This base material is the structural component of the laminate which must resist stresses imposed by playback or storage without permanent deformation and maintain dimensional stability during aging. That these thin films perform this mission as well as they do is somewhat surprising because they are, after all, thermoplastics subjected to severe loading conditions.

The severe loading conditions imposed by storage are:

(1) The forces caused by winding the tape under tension. This creates high radial pressures in the roll of tape which diminish in intensity from the hub outwards. This radial pressure causes longitudinal warping and any unevenness in stress distribution in the roll, such as is caused by hub slots, splices, or poor wind result in localized permanent deformation which impair playback qualities of the tape.

(2) The forces caused by the difference in properties between the film base and the coating. These may be differences in thermal or humidity coefficients of expansion or differences in dimensional response to aging. This can cause curl (transverse warping of the tape).

(3) The forces caused by the boundary conditions. The edges of the tape are exposed to the environment while the center is not. If the tape is not in equilibrium with its environment, the dimensional changes induced by the gradient will vary in amount from the edges towards the center of the tape. This can cause curling or edge fluting.

In addition to these forces, dimensional changes are induced by the recovery of molecular configurational strains (which result from the film fabrication process and are the same kind as those discussed under plastic discs), gross changes in winding tension induced by aging or changes in humidity or temperature, and simple relaxation of elastic stresses. The reason that these dimensional changes are so important is that satisfactory reproducing response is dependent on the surfaces of the reproducing head and tape being in perfect contact and the edges of the reproducing head gap being aligned (with reference to the tape) correctly with the original alignment of the trailing edge of the recording head gap. Variations in either of these parameters cause fluctuations in signal amplitude whose seriousness increases with increase of frequency. These effects have been so thoroughly measured and reported by different investigators (see Daniel, Axon and Frost, (48) Westmijze, (78) or Bulletins No. 6 and No. 27 of 3M Sound Talk (82) that complete quantitative data were not taken on signal attenuation as a function of head and tape separation or misalignment. An example of the seriousness of this parameter is that a 7,500 cps signal on a half track 7½ inches per second recording is attenuated about 6 db by a head and tape separation of only 0.1 mil or a head and tape misalignment of only ⅓ degree. Figure 22 shows the relationship of this type of attenuation to other parameters and the effect of equalization on playback.

It is primarily in dimensional stability that Mylar is superior to cellulose acetate and that thicker bases are superior to thinner bases. This stability is, of course, affected by the coating which is a different plastic from the base and highly filled with iron oxide and so exhibits different dimensional changes than does the base. Comparative figures obtained from manufacturer's laboratories (3M(83) and Du Pont (117)) for storage conditions are:

	¼ inch Acetate Tape	¼ inch Mylar Tape	Mylar Film
Thermal coefficient of Linear expansion	3.0	2.0	1.5×10^{-5} ''/''/°F.
Humidity coefficient of Linear expansion	15.0	1.1	1.1×10^{-5} ''/''/% R.H.
Creep (7000 psi tension for 3 hours and 3 hours recovery)	0.015	0.005	''/''/ at Ambient.

Frequency (cps)
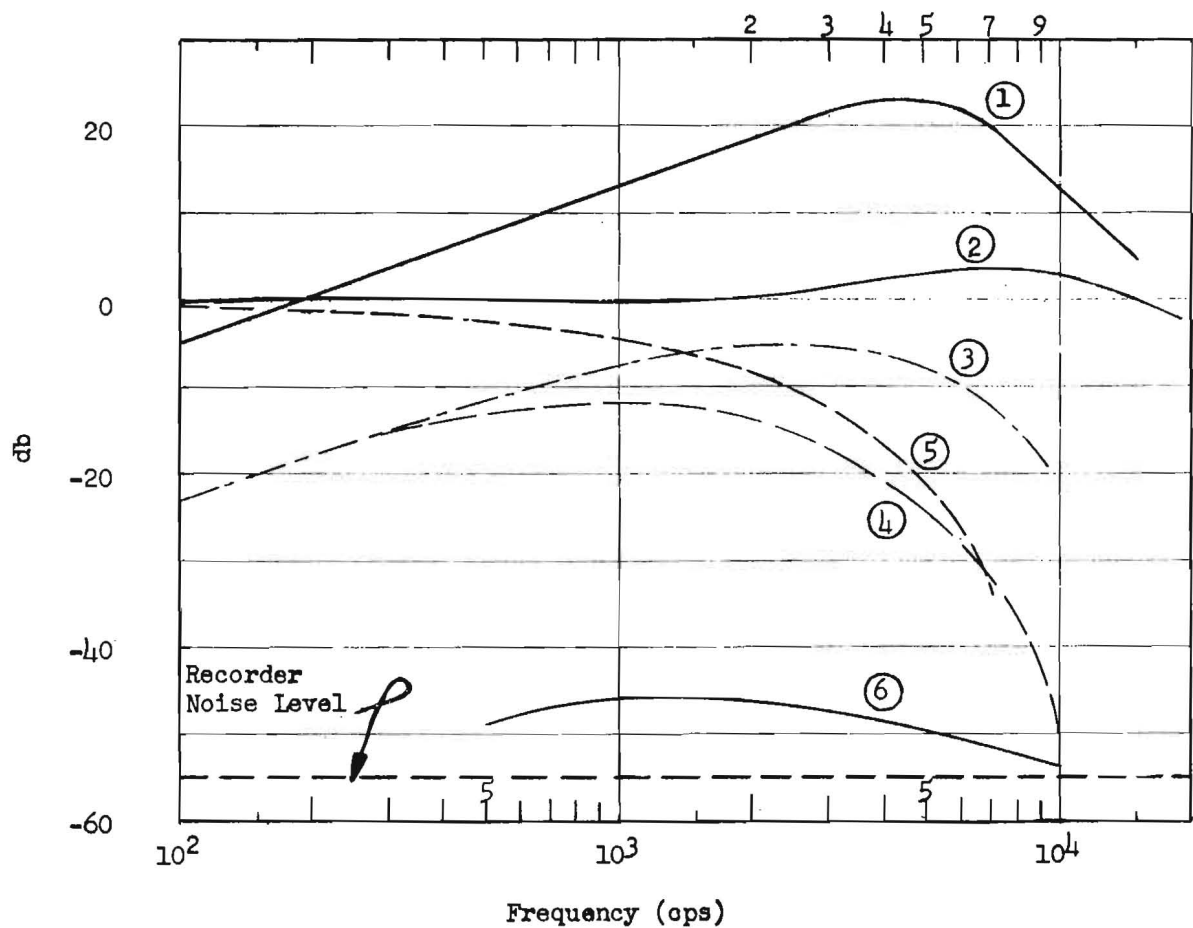
1   Actual Tape Output—Constant Power Input
2   Recorder Output—Equalization
3   Actual Tape Output—Tape 1 mil from Head
4   Actual Tape Output—Tape 2 mil from Head
5   Recorder Output—Tape 1 mil from Head
6   Print Through (Estimated 20 year level from Daniel & Axon data) for good storage conditions

Figure 22.   **Characteristic data for a general coated, 1.5 mil tape showing the interrelationship of various parameters (actual values depend on tape and recorder), tape speed 15 I.P.S.**

A further difference between these two base materials is that the moisture absorbed by cellulose acetate acts as a secondary plasticizer affecting its impact strength (brittleness), its tensile modulus of elasticity (elongation under load), and its creep (residual elongation after removal of load). Mylar absorbs less than $\frac{1}{2}\%$ by weight of water and its physical properties are unaffected by change in environmental humidity. Mylar has the defect of stretching under impact loads (which would merely break acetate) that are caused by a poorly operated or adjusted machine which means that more supervision must be exercised over playback equipment use than is required for acetate.

The storage techniques indicated by these properties of the base are:

(1) The use of metal, unslotted hubs of as large diameter as possible.
(2) The use of constant torque* winding using as low an initial tension as is compatible with producing a well wound pack.
(3) The use of reel flanges which are not deformed out of plane.
(4) As perfect a winding pack as can be obtained.

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*Constant tension winding not only results in higher radial pressures, it results in slippage of already wound tape layers with consequent localized stress distributions.

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(5) The inhibition of changes in environmental humidity and temperature.

Since it takes a very long time for a reel of acetate tape to come into equilibrium with a large change in environmental moisture content, this last requirement is most important for acetate tapes. The recommended procedure for accomplishing these ends is to keep playback and packaging rooms at 70° F and 50% R.H. Tapes received for storage should be rewound in the packaging room on a rewind machine using a constant torque drive with a tension of from 3 to 5 ounces for $\frac{1}{4}$ inch wide 1.5 mil thick tape at the hub of a N.A.R.T.B. 10 inch reel and whose maximum speed is 30 inches per second. The reel used should be metal, with undeformed flanges, having an unslotted hub of the N.A.R.T.B. 10 inch reel design. Acetate tape which has been exposed to other than the recommended environment should remain unpackaged in the conditioning room for six weeks and rewound; after inspection of the tape to make sure that the winding is satisfactory, the tape should be packaged in a metal can or a box made of the type of laminate material recommended for packaging discs, and the package sealed. The boxes or cans should be stored on edge so that the flanges will not be deformed by gravity loads such as might happen if they were kept in horizontal stacks.

Cellulose acetate base has been used for a long time, in safety motion picture film for example, and is known to have a dependable and long storage life. Mylar has been used for a much shorter time but has a theoretically longer storage life, mainly because no plasticizer or modifiers are used in its formulation.

C. Binder

The magnetic tape coating binder is the most critical part of the tape from the standpoint of aging. Unfortunately, it is the component about which the least information is available because the coating formulations are carefully guarded trade secrets. The early tapes (prior to 1950) often failed by aging in as short a period as five years because of chemical or physical degradation of the binder which was manifested by delamination or blocking (layer to layer adhesion). The binder must perform several very difficult roles. In the manufacturing process it must be susceptible to providing very complete dispersion of the iron oxide and to depositing a remarkably uniform coating of the mixture by solvent release without solvent

attack on the base. The final product must furnish a smooth and tough surface which will not erode or rub off during playback or adhere to adjacent base material under the influence of the high radial pressures which are induced by winding under tension. The binder must adhere so firmly to the base material and the iron oxide that it will resist the stresses of playback and storage without crazing, flaking, or peeling. Furthermore, it must maintain these properties despite loss of residual solvent, and possibly, plasticizer as well as chemical degradation.

An early binder resin used was cellulose nitrate which proved to have excellent adhesive properties but, as has been noted, (103) (122) (123) has poor aging qualities. Presently, it is believed, chlorine bearing vinyls are much used. These resins exhibit only fair adhesion to cellulose acetate, but this can be enhanced by such mechanisms as the use of a wash primer of polyvinyl butyral which is hydroxyl bearing. (113) Other mechanisms which may be used for enhancing adhesion are solvent attack and controlled oxidative degradation of the base surface. These resins have good aging qualities but the catalytic effect of iron on the thermal decomposition of these resins as well as the change in properties associated with loss of plasticizer leave the potential longevity of these coatings somewhat questionable. Another currently used binder is believed to be an internally plasticized acrylic resin. It offers a longer theoretical potential storage life although no data are available to confirm this.

In addition to these binder materials, other film forming materials have doubtless been studied and are, perhaps, in use. Of these materials, the epoxy resins show great promise. Regrettably, these critical materials cannot be properly evaluated with the data at hand, and those most able to make such an evaluation, the research chemists of the tape industry, cannot freely communicate their knowledge because it represents a real asset of their organizations which would be lost by such communication. The art of the manufacture and use of synthetic resin coatings is still in a state of rapid development and one can expect that far superior coatings to the presently used ones will be available in the foreseeable future. It would be a worthwhile endeavor, indeed, if the tape manufacturers would cooperate in the endeavor to develop a binder formulation with optimum aging properties with disregard for the other properties, such as cost, which are of importance in the competitive marketing of tape. The obstacles to such cooperation are fully

recognized but the end results would be of great benefit to all.

One aspect of binders cannot be separated from the nature of the base material and that is coating to base adhesion. Because of the difference in chemistry between the two materials, it is more difficult to obtain good bond between most coatings and Mylar than it is between those coatings and cellulose acetate. The initial bond obtained by present tape manufacturing techniques is excellent, but the experience with the response to natural aging is not as extensive in the case of Mylar as it is in the case of cellulose acetate. This poses another question to which no answer is available at this time; that is, does the possibility of premature delamination of Mylar base tape outweigh the advantages which Mylar has over cellulose acetate? Greater experience with and knowledge of these materials is required to choose properly between these materials for long-time storage requirements.

Because these coatings are deposited by solvent release and residual solvent affects their properties, it is desirable to "age" tapes for a period of six months prior to inspection and recording on them for long-time storage. Such "aging" should be done in the conditioning room and should disclose manufacturing defects not noticeable in the new tape. In the course of this project, a number of random tape failures by loss of bond between coating and base or transfer of coating to adjacent layers were observed after aging which were not present when the tapes were received. These tapes were stored at approximately 70° F. and 50% R.H. in their original containers. It is believed that the evaporation of residual solvent was responsible for the disclosure of these defects.

D. Iron Oxide

The base material and binder are used for only one purpose, to keep the iron oxide particles in place. This iron oxide is manufactured by a careful process of dehydration and reduction of $Fe_2O_3.H_2O$ to Fe_3O_4. Fe_3O_4 is black magnetite used in high output tapes and many of the earlier tapes. At present, most tapes use the reddish brown gamma ferric oxide produced by oxidizing Fe_3O_4. The end product must be very carefully washed to remove all traces of acid used in the process as acids are uniform catalysts of degradation for most of the thermoplastics presently used as binder resins. Many premature failures of older tapes can probably be attributed to use of acid iron oxide.

The reason magnetic powder is superior as a recording medium to a continuous magnetic material is provided by the domain theory of magnetism which also is the basis for the theories of changes in magnetization during aging. In this theory, a magnetic material is considered to be divided into domains within each of which the local magnetization is saturated (each domain is a magnet). The resultant magnetic moment of a piece of this material is dependent on the size and orientation of these domains. Figure 23 is a schematic simplification of this theory. The size and interaction of these domains exert a great influence on the response of a magnetic medium and the best way to control this parameter is to use powders with the most desirable powder consisting of sufficiently

1. In an unmagnetized piece the domains balance out
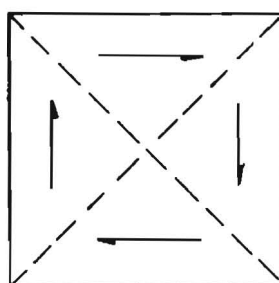
2. A piece may be magnetized by changes in domain size
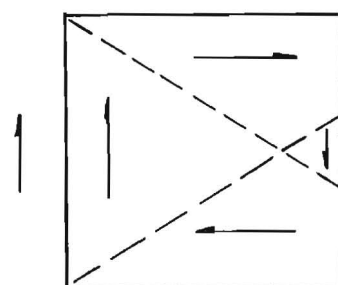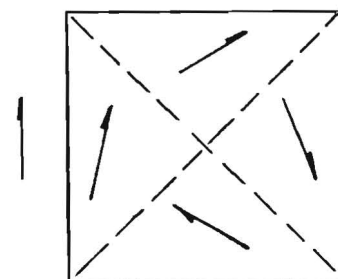

3. Or by domain rotation

Figure 23. **Magnetic domains (after Kittel) (61).**

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small particles, each composed of a single domain. If a small particle is forced to remain as a single domain, it will not be possible for magnetization changes to take place by boundary displacement which usually requires relatively weak fields, but such changes must be induced by domain rotation which requires large fields. In such powders, the important parameters are size, shape, orientation and separation of the particles. The uniformity of distribution, size and orientation of the iron oxide in magnetic tape is therefore exceedingly important in determining its quality, and the particle size, shape and separation determine its high frequency response as well as other magnetic properties.

The basic theory backed up by very thorough experimental work by a number of investigators whose results are in substantial agreement form the basis for the following conclusions (see Westmijze (78), Daniel and Axon (47), Herr and von Behren (56), Latham (63), Sound Talk Bulletin No. 10 (82), and Radocy (67) (68) (69)) which were verified by the duplication of experiments reported by the original investigators. The changes which occur in signal during long-time storage are demagnetization and the introduction of magnetization other than that originally recorded on the tape.

Tape demagnetization can be dismissed fairly easily. It does occur, but is primarily a weak field magnetization (high frequency) phenomenon, and if a magnetic tape is properly recorded and is kept in the proper environment, the amount of attenuation will not be noticeable. One can expect a slight decrease in signal to noise ratio in very long-time storage, but tape provides such a large initial signal to noise ratio that this is a minor effect (this remark applies to storage demagnetization only).

In the absence of large external fields, the introduction of other than recorded magnetization is limited to print-through (the magnetization in one layer of tape inducing magnetization in adjacent layers). Print-through is probably limited to magnetization by domain boundary displacement which, as has been noted, is associated with relatively weak fields and requires more than one domain to exist in the magnetic particle. The domain boundaries have preferred positions separated from each other by potential barriers which vary in magnitude. The boundaries obtain energy from the lattice which enables them to surmount the potential barriers; the attainment of equilibrium (positions of lowest energy) is dependent on the magnitude of the potential barrier and the probability of a boundary obtaining the requisite energy to sur-

mount it. This can be accelerated by increasing lattice energy by an increase in temperature or by making the height of the potential barrier oscillate by introducing an alternating field. The field of adjacent tape layers increases the potential energy of the boundaries and results in a biased redistribution of boundaries which increases the mean magnetic moment in the direction of the field. Removing the field results in a redistribution of boundaries in the direction of the original preferred distribution.

In terms of magnetic tape, this means that the intensity of print-through depends on potential barrier height and boundary energy which are influenced by:

(1) Temperature.

(2) Strength of master field and its distance from the slave particles (which also makes print-through a function of wave length).

(3) Time of contact and time of separation.

(4) External A.C. fields.

(5) Size, shape, and orientation of magnetic particles.

It also means that the temperature, time, and intensity relationships should obey diffusion laws defined by the theory of probability.

In practical terms, the conclusions arrived at by theory and experiment are:

(1) The strength of the slave signal is practically proportional to the strength of the master signal. In order to obtain optimum signal to noise ratio together with satisfactory signal to print-through ratio, all material should be recorded below 2% harmonic distortion (4 db down from normal recording level is a usual figure). Recording at lower levels does not improve signal to print-through ratio while it reduces signal to noise ratio.

(2) Print-through intensity increases with time of contact of master and slave and decreases with time of separation. The rate of measured increase or decrease in db of print-through diminishes logarithmically with time. While print-through does not actually approach a limit, it is an asymptotic function which is bounded for finite times of the order of tape life expectancy. This permits the prediction of print-through intensity to be made from short-time tests. Tape inspection procedure should include the measurement of print-through and the prediction of length of time required for print-through intensity to reach the maximum tolerance level. Figure 24 depicts this relationship. Also see Figure 25.

(3) Print-through intensity is a function of signal wavelength (in mils measured on the tape). Maxi-
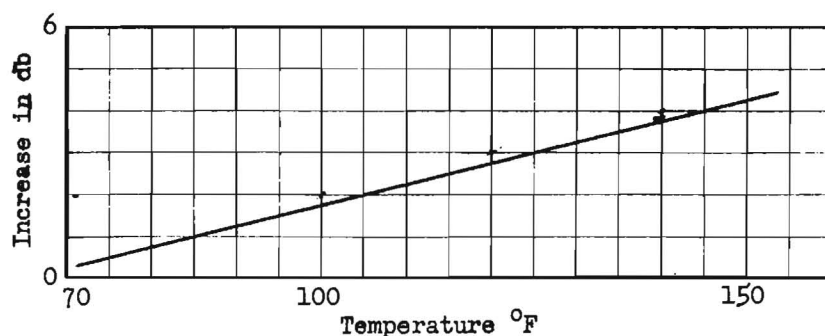
Print Through as a Function of Temperature
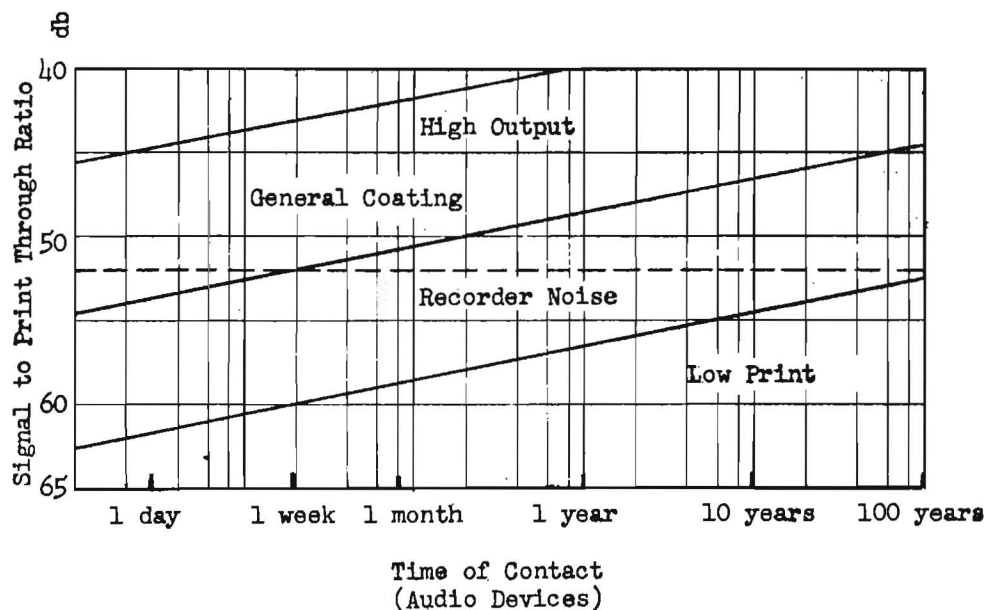7.5 ips; 400 cps; 3% Total Distortion
(Audio Devices)

Time of Contact
(Audio Devices)

Figure 24.

mum print-through is obtained from the 10 to 20 mil wavelength (about 1200 cps for 15 ips or 600 cps for 7½ ips). It is recommended that print-through surveillance be performed on a recorded tone burst of about 10 mil wave length on each tape at the maximum recording level of the tape for inspection purposes.

(4) Print-through intensity is a function of environmental temperature. For this reason it is desirable to keep environmental temperature as low as is compatible with other requirements (see Figure 24).

(5) Print-through intensity is increased by exposure of tape to external A.C. fields (while slave is in contact with master) of sufficient intensity and duration. It is believed that stray external fields below 10 gauss will not cause noticeable changes.

(6) Print-through intensity is a function of coating and base thicknesses. The thickest base tape feasible should be used.

(7) Print-through intensity is a function of the uniformity, size, shape, and orientation of the magnetic particles. In recent years, improvements in manufacture have resulted in coatings which exhibit far less print-through than older materials. Theoretically, there is no limit on the improvement of print-through characteristics which can be achieved by magnetic particle improvement and it can be expected that much improvement will be made in the future (such improvement will also benefit high frequency response).

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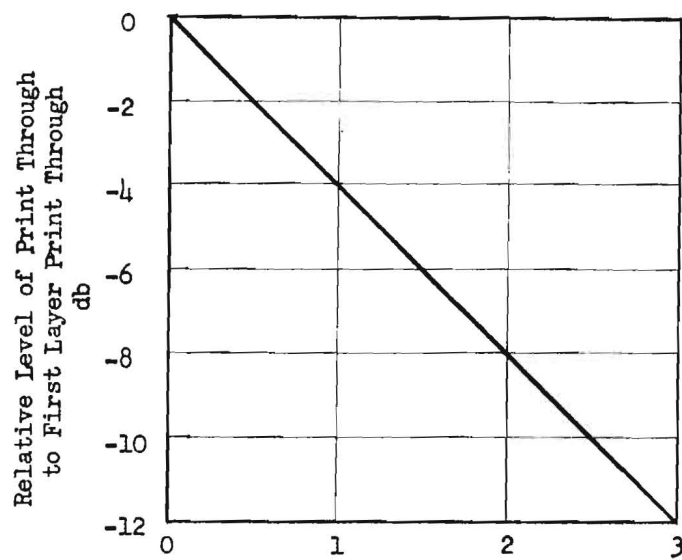
Number of Layers Between
Master and Slave
(after Daniel & Axon)
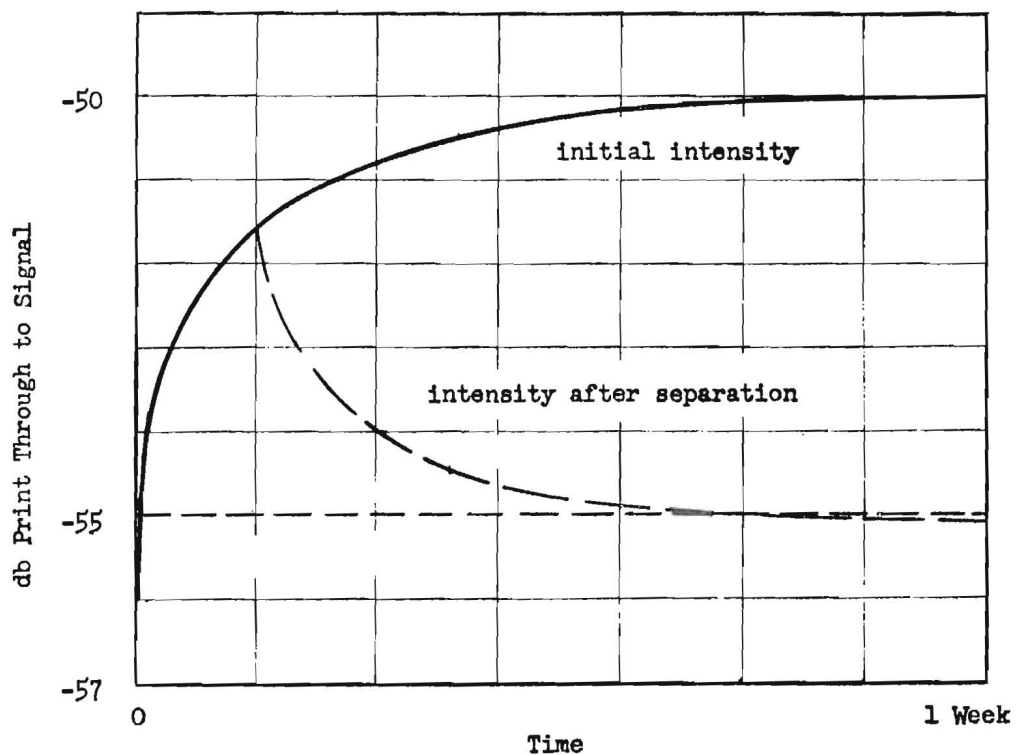
Typical Print Through Curve
Ambient Temperature; 1000 cps; 15 ips
1½ mil General Coating Tape

Figure 25.

(8) Print-through decay can be accelerated by exposing the tape to A.C. fields when slave is not in contact with master (selective erasure). This will also cause attenuation of other weak field magnetization (such as high frequency signal). Selective erasure is a valuable curative measure for tape recorded at too high a level or which has been exposed to high temperatures or A.C. fields; in particular, just prior to re-recording. It should not be used indiscriminately or carelessly. Selective erasure is best accomplished by using a coil through which the tape is passed at recording speeds with reduced erase current from a recorder. Figure 26 is a graph made of the attenuation of print-through and signal induced in a general coating type by using an erase head and a potentiometer controlled erase current of 100,000 cps. The measurement is ratio of original signal (or print-through) to attenuated signal (or print-through) as a function of erase current. It can be seen that there is a net gain in signal to print-through ratio and an optimum value of the erase current for this single frequency. Unfortunately, the attenuation of very high frequency signal would be much greater than of the test signal. As Westmijze has noted, this can be provided for by a change in equalization with a loss of signal to noise ratio. This all adds up to a critical process justified only in unusual cases in library operation.

E. Conclusions and Recommendations

In summary, print-through does not need to be a problem. Use of proper tape, proper recording level, proper storage environment, and proper surveillance will keep print-through below the tolerance level. In those cases where the library has not had control of these parameters, an undesirable intensity of print-through may develop. In many cases, the recording can be salvaged by curative measures such as selective erasure. A further advantage can be obtained by the future development of magnetic powder coatings far less susceptible to print-through than even the best currently produced coatings.

The recommended procedure for storing magnetic tape is to:

(1) Use only metal reels with an unslotted hub of N.A.R.T.B. dimensions (10″ reel size). The flanges of these reels must be replaced if they are deformed out of plane.

(2) Package reels in sealed metal cans or sealed boxes of a material such as polyethylene/cardboard/foil/polyethylene laminate. The boxes should be
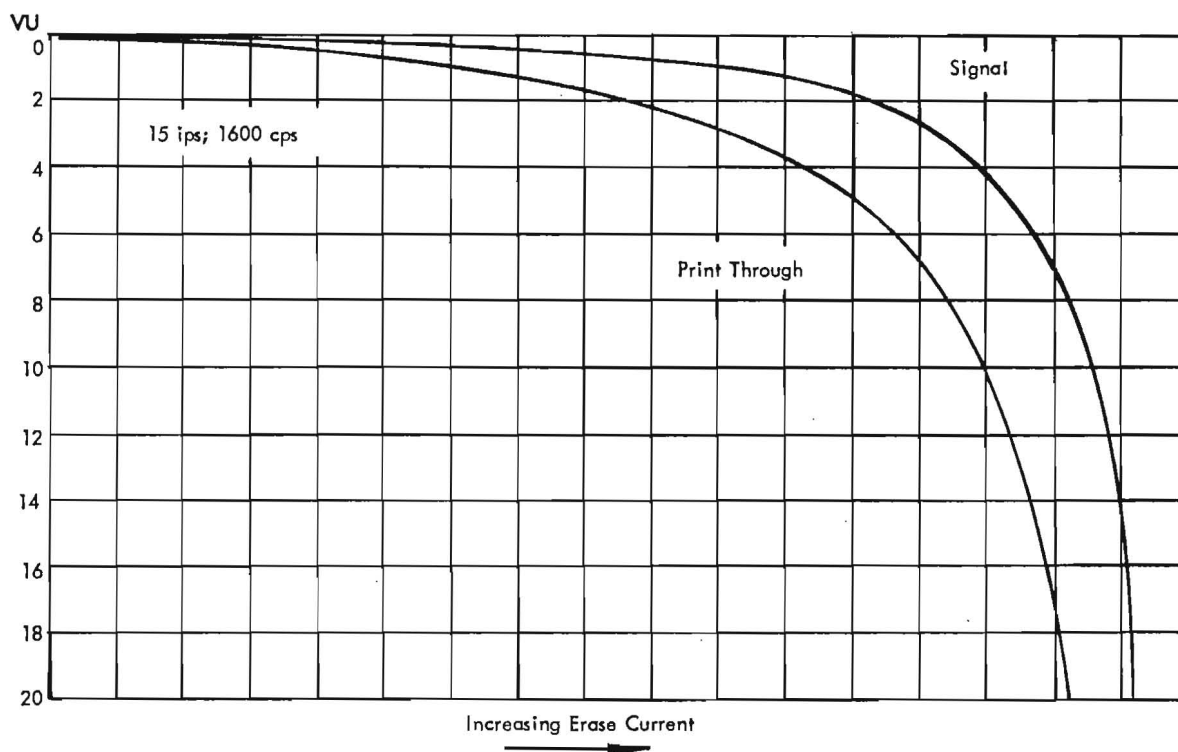

Figure 26. Selective erasure graph.

stacked on edge in the shelves. Tape should not be packaged until it is in equilibrium with 70° F and 50% R.H.

(3) Stack temperature should be maintained at a temperature of 70°±5° F for often used recordings, and storage in special vaults at 50°±5° F is recommended for seldom used and valuable recordings. Stack humidity should be kept at 50%±10% R.H. if this is feasible.

(4) Playback and packaging rooms should be maintained dust free and at 70°±5° F and 50% ±10% R.H. Tapes exposed to other environments should be conditioned in the playback environment before playback.

(5) Stray external magnetic fields should not be permitted in the stack, playback and packaging environments. The maximum flux density permitted should be 10 gauss. It should be remembered that all current bearing wires have associated magnetic fields. Ordinary electric circuits, if properly installed and balanced, will cause no trouble because the fields will "cancel out."

(6) Playback equipment should be maintained as recommended by the manufacturer. This includes cleaning, tape transport adjustment, and component demagnetization.

(7) A rewind and inspection deck, separate from playback facilities, should be used for packaging and inspection. Winding tension for 1½ mil tape should be constant torque of 3–5 ounces at the hub of a 10 inch N.A.R.T.B. reel.

(8) The best tape presently available for storage purposes appears to be 1½ mil Mylar base with some doubt existing as to the coating to base adhesion of this type of tape. Any of the tape manufacturers are presently capable of producing longer lived tapes if there is sufficient demand for them and it is hoped that one or more of them will do so. Each of the major manufacturers produces good tape and each product seems to have a slight advantage over the others in one parameter while being at a slight disadvantage in others. The competition in this market is enforcing rapid advances in tape construction and formulation which should result in tapes of superior potential longevity in the foreseeable future.

(9) Tape should be recorded at a maximum level below 2% harmonic distortion (4 db below normal recording level is usually satisfactory). The first and last fifteen feet of the tape should not be used for program recording but should have a burst of 10 mil wavelength (approximately 750 cps at 7½ ips) signal at maximum recording level preceded and followed by several layers of blank tape for inspection purposes. Tape should be aged in the packaging room for six months prior to recording. Recorded tape which has been exposed to other than the prescribed environment should be conditioned in the packaging room for six weeks prior to packaging.

(10) Tape should be inspected once every two years measured from time of last playback and rewound so that the curvature of the base is opposite to the direction of the previous curvature. This inspection should consist of measurement of print-through caused by the toneburst at the end of the tape and a spot check at the tape end next to the hub for coating adhesion or delamination. It need not include playback.

The benefits of rewind are in reduction of creep induced curvature and print-through. The disadvantage is in exposing the surface to oxidative attack. The tape should be inspected and wound after each playback.

(11) Storage shelves should be of wood or a non-magnetizable metal free from vibration or shock.

(12) The same care in procurement and shipment should be taken with tape as was recommended for discs.

V. RECOMMENDATIONS FOR FUTURE WORK

Sound recordings are cultural assets worthy of preservation. In the development of sound recording media, potential longevity has been a consideration secondary to such parameters as fidelity of reproduction and cost of manufacture. Because potential longevity is a property which is incorporated into an article when it is manufactured, all that can be done with an existing sound recording is to keep it in the environment most conducive to attainment of its maximum life and to re-record it before failure. Unfortunately, neither the life span of these materials nor the criteria for detection of incipient failure are known. This requisite knowledge could be obtained in a relatively small number of years by appropriate studies. The best approach would not consist of a concentrated effort to measure the parameters of interest but of a five to ten year study of aging under mildly accelerated aging conditions. Such an effort would consist of:

(1) A large number of unattended but monitored accelerated aging tests of several years duration using moderately elevated temperatures and variation in humidity and aeration. An individual test would require the expenditure of but small amounts for equipment, space, and manpower. The results of such a program would yield information of value not only for the manufacturers and collectors of sound recordings but for all concerned with the degradation of plastics.

(2) Stack surveys of existing collections measuring sound recording degradation as a function of changes in material chemistry. As has been noted in chapter III A and III C there is a group of simple chemical analytical techniques which should predict incipient failure of sound recording materials. The data necessary for correlation of these changes to degradation could be collected by such surveys.

If a committee of interested people were organized for these purposes and the services of a consulting research organization were engaged to coordinate and evaluate the work done by the committee, the costs would not be prohibitive to acquire the information which would reduce the costs of surveillance of sound recording collections and provide increased security against loss of sound recordings. The objectives of such a study would be:

(1) To determine the maximum times for which the different types of sound recordings can be safely stored without surveillance.

(2) To determine surveillance techniques to be used for establishing necessity for re-recording.

(3) To establish the most economical environments and storage techniques for sound recordings.

The aforementioned recommendations were pointed towards the economical preservation of existing sound recordings. For the future, it is desirable to have more stable media of longer life and less dependence on expensive storage environments and techniques. The present state of knowledge should permit manufacture of sound recordings of several times the potential life of currently used media. If there is sufficient demand for longer lived sound recording materials, and this can be proven to the industry, they will, undoubtedly, develop and produce such materials. If such demand does not exist, the cost of development and production of longer lived materials must be borne by those few who will benefit from such endeavor. Even in this latter case it would be unthinkable not to take advantage of the wealth of knowledge which has been accumulated by those in industry, which is largely unavailable at the present time because of the necessity for preservation of trade secrecy. Such a project would involve public relations as well as the cooperation of many people of such diverse disciplines as library science, solid state physics, sound recording, plastics technology and chemistry. If one were to adopt successful precedent, the formation of a Committee for the Preservation of Sound Recordings is indicated. Such a group formed of people with a mutual interest in the problem and with the

desire and ability to contribute to the development of longer lived sound recordings could achieve dramatic results in this field which would not be attainable by any single research effort or organization of limited viewpoint. The main obstacle to progress in this field seems to be the lack of communication between the different disciplines and this should be easily overcome by such an approach.

NOTE.—For this report, it has been necessary to summarize the original data and present them in tabular and graphic form. The original data, recorded on microfilm, may be obtained upon request from the Library of Congress.

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EQUIPMENT USED FOR THE ACCELERATED AGING OF DISCS AND INSPECTION PROCEDURE

The purpose of these tests was to determine what changes in playback quality resulted from the chemical and physical changes of shelf aging. Equipment used to accelerate changes was:

(1) A Sub-Zero Constant Temperature Cabinet (American Instrument Company—Type Z) which was used for exposure of discs to temperatures below ambient.

(2) A gravity convection laboratory oven (Blue M Electric Company—Blue Line OV–18) which was used for exposure of discs to temperatures above ambient.

(3) An air circulation and humidity control chamber (a 21 quart aluminum canning sterilizer purchased from a hardware store) in which the specimens were sealed before placement in the oven. Two rubber laboratory hose connections were attached to the chamber and brought outside of the oven to permit control and examination of the environmental atmosphere. Such a chamber is a required accessory for ordinary laboratory ovens if proper temperature, air circulation and humidity control are to be achieved.

(4) A portable precision potentiometer (Rubicon No. 2732) used with Copper Constantin thermocouples for temperature measurement of disc surfaces.

(5) A portable humidity indicator using Minneapolis-Honeywell Elements O229A1 through O229A11 (see Applied Research Project 4799, Report I, Minneapolis-Honeywell Research Division, 500 Washington Avenue South, Hopkins, Minnesota for complete description of instrument). Humidity control was achieved by the use of evaporating pans containing saturated salt solutions.

(6) A Westinghouse C–H5 Mercury lamp with reflector housed in a steel cylinder which contained an air circulation system to keep specimen at room temperature. The ultra violet radiation of this lamp induces photo chemical reactions which often accelerate the initiation of chemical degradation in organic materials. This U.V. exposure was used in an attempt to shorten the induction period of natural aging reactions.

The discs were inspected before, during, and after aging by the following methods:

(1) Visual examination, including microscopic examination of grooves and lands.

(2) Weighing to 0.01 grams after 12 hours of conditioning at standard conditions (50% R.H., 70° F).

(3) Noise measurement. An important parameter of disc degradation is decrease in signal to noise ratio caused by changes in the smoothness of groove wall surfaces. Possible causes of such surface changes are microcracking, spalling off of material and dimensional changes induced by stress relaxation (39) or chemical degradation. In order to measure changes in noise, the unmodulated groove disc specimens were used and electronic equipment assembled as shown in Figures 27, 28, and 29.

The noise measurements to be made consisted of (1) counting of the noise spikes that reached a predetermined level of voltage and that occurred within a ten revolution period of a record, and, (2) the integration of all of the noise under a predetermined level of voltage that occurred within the same ten revolutions. The total noise signal was picked up from the record by the pickup which was connected into a preamplifier whose output was
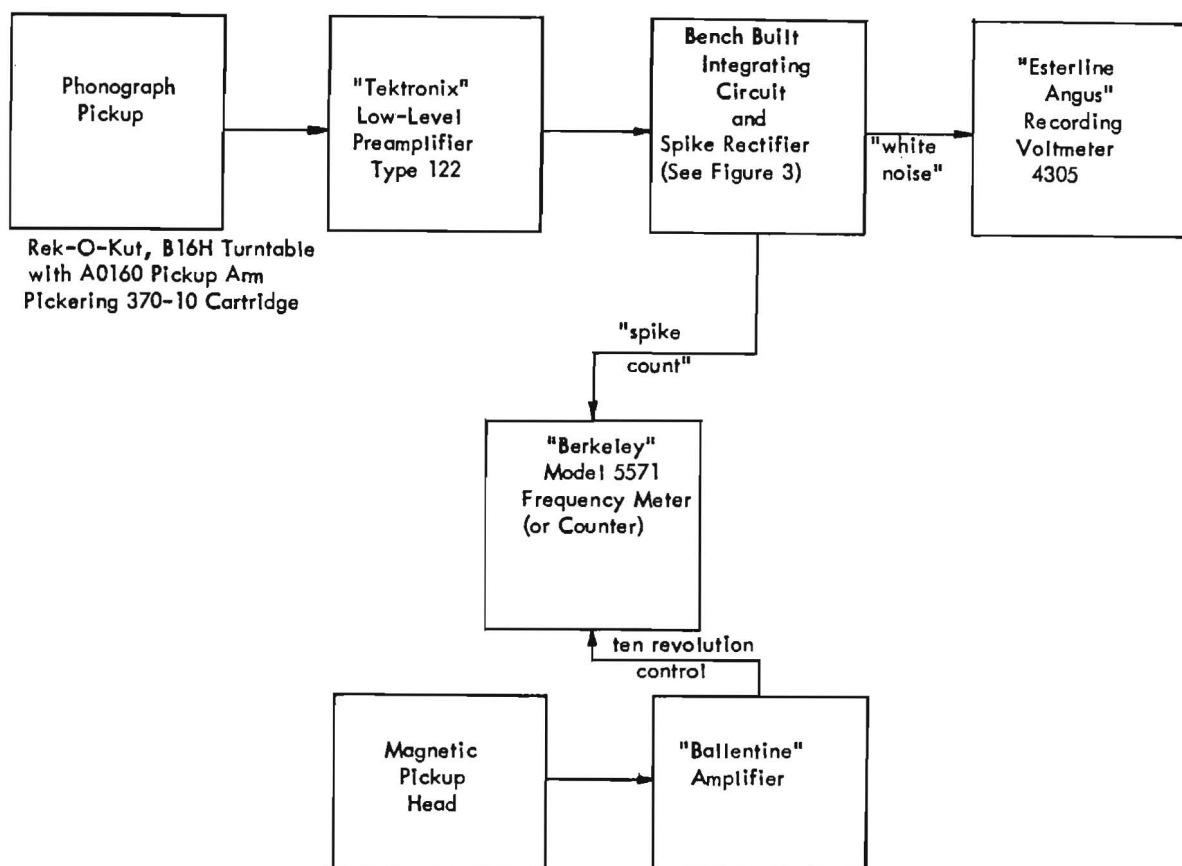
Figure 27. Block diagram of noise measuring equipment.

connected to a phase inverter circuit. One signal path, after the phase inverter, was through a rectifier circuit to a jack that lead to the pulse counter. The other part was through a limiting circuit to a gate tube, through a transformer to a full wave rectifier, and from there to an integrating circuit. The output of the integrating circuit was connected to the grid of an amplifier tube, and an Esterline Angus recorder was connected in the plate circuit of this tube to give an indication of the integrated noise.

The counter had controls that allowed it to count everything that was lead into one input between a voltage excursion at the other input and the tenth following excursion. The eleventh excursion then started the count over again. To provide the pulses for starting and stopping the counting operation, a small magnet was attached to a point on the rim of the turntable, and a magnetic pickup head was located in such a position that it would have a voltage induced into it with each revolution of the turntable. This pulse output was connected to the input of a Ballentine amplifier which amplified

it to a level that would trigger the counter circuit. This method provided a period of measurement of ten revolutions of a record. A positioning arm was made that would provide a method of positioning the stylus in the same groove of the record each time that the record was tested.

The gate pulses were fed into the integrator circuit through a cathode follower probe that was connected into the counter unit. These pulses were used to operate an interlock relay system that in turn caused the integration circuit to begin operation. After the tenth pulse cut the circuit off, the relays were locked in such a position that a reset button had to be pushed before the circuit would begin summing again. This feature was added to keep the eleventh trigger pulse from starting the summing operation again before a reading of data could be made and the integrator capacitors discharged. A pilot light indicator was connected to one of the relays in such a manner that it would give an indication as to when the circuits were counting and integrating. This feature was put on the equipment in order to alert
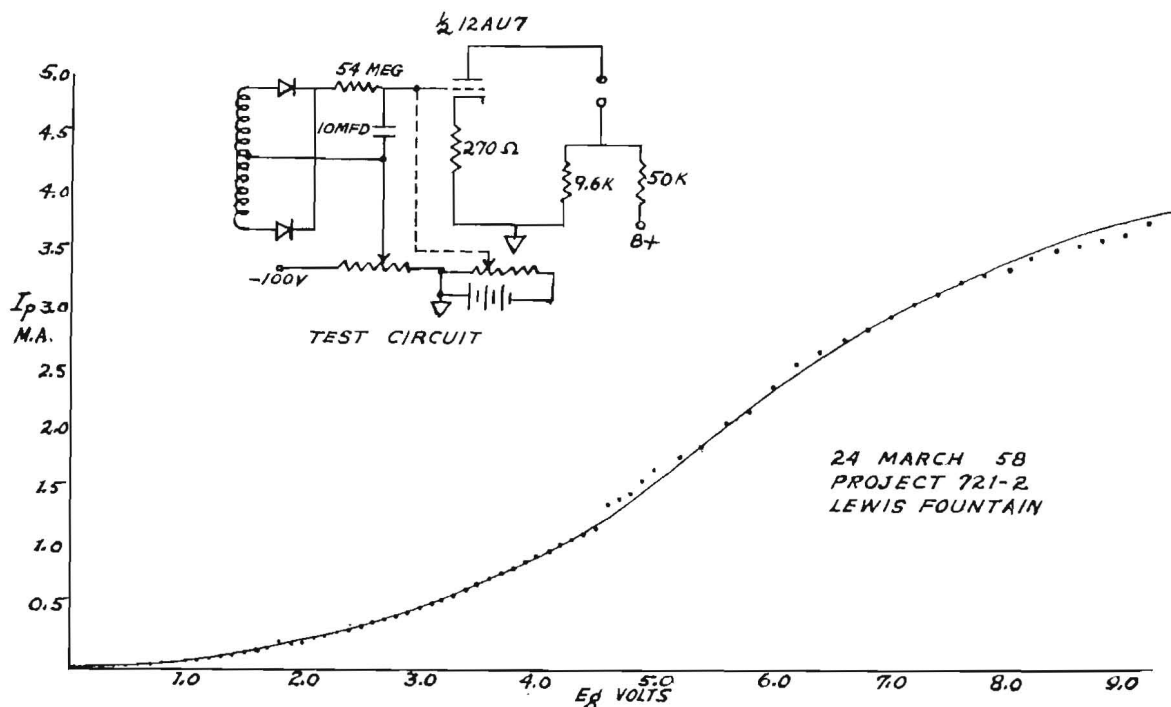
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Figure 28. Noise integrator and spike rectifier circuit.

Figure 29. Integrated noise (capacitor voltage) vs. output current.

the operator so that he would know when to take his reading from the counter.

1. OPERATION

The operational procedure was as follows in the order given:

(1) Turn on the counter unit and allow at least twenty minutes for warmup.

(2) Turn on the Tektronix preamplifier, the Ballentine amplifier and both power supplies for the integration circuits.

(3) Position the turntable so that the small magnet that was on the rim was in such a position that the turntable had to make at least ¾ of a revolution before the magnet could pass in front of the magnetic pickup head.

(4) Place the pickup on the record in the desired position using the pickup positioning arm for exact placement.

(5) Push the reset button on the counter.

(6) Turn the Multiplier switch that was located on the integrator chassis to "Discharge" and then back to the desired range for measurement.

(7) Push the reset button on the integrator chassis.

(8) Start the turntable.

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(9) Immediately take the reading on the counter when the indicating light goes off.

(10) Mark identifying information on the recorder chart.

2. CALIBRATION

a. *Diode Limiter Bias in Integration Circuit.*

The transformer that was used in the integration circuit started to distort noticeably when a 1000 cps sine wave signal of 27.5V RMS was applied to its primary. A signal of 0.5 volts RMS or 0.707 peak-to-peak on the grid of the 6AK6 driver tube caused a signal of this size to appear across the primary. The limiting diodes were biased at a point that caused them to start clipping at this voltage. To accomplish this, the following operating procedure was used:

(1) Feed a 1000 cps sine wave signal into the input of the integration circuit, and with the gain control in a full clockwise position and an oscilloscope connected to the grid, pin 1, of the 6AK6 driver tube, observe the waveform.

(2) While increasing the signal amplitude, adjust the diode bias controls for maximum bias, which was indicated by the maximum signal that could be fed in without clipping.

(3) Connect the oscilloscope to the plate, pin 5,

of the driver tube, and turn the signal gain down until distortion just begins to appear.

(4) Adjust the diode bias controls until both top and bottom of the waveform begin to be limited.

b. *Output Tube Bias.*

With no signal into the integration circuit and with the storage capacitors discharged, the bias control was adjusted until a 0.5 ma. reading was obtained on a milliammeter connected to the output jack. A curve that was plotted for the output tube shows that this setting gave the most linear output from the tube.

c. *Counter Adjustments.*

Exploratory tests showed that some noise spikes reached 10 mv or higher, so a nominal value of 5 mv was chosen as a starting level for the spike counting. This would be 3.5 volts RMS after amplification. The following operating procedure was used for counter adjustment:

(1) Connect the output of the Ballentine amplifier to the "B" input of the counter.

(2) Set the "Function" switch to "Count".

(3) Put the "B Slope Switch" to "+".

(4) Start the turntable, and adjust the "B Attenuator" and "Trigger Level" adjustment on the counter and the gain switch on the amplifier until a dependable count was obtained.

(5) Set the "Function" switch to "$\underline{A} \times 10$."
$$\overline{B}$$

(6) Feed a 3.5 volt RMS signal from a signal generator into the "A" input, and with the turntable signal still triggering the "B" input, adjust the "A Slope Switch" to "+"; adjust the "A Attenuator" switch and "Trigger Level" control until the counter just began to count.

(7) Adjust the "Display Time" control to a position that would cause the display to last less than the time of one revolution of a record.

(8) Disconnect the signal generator, and connect the output of the Tektronix amplifier to the "A" input of the counter.

The equipment was now ready for operation. The "A" controls were left in the above positions for the duration of a test series. If they had been moved, the 5 mv peak counting level would have been void.

The equipment now counted all noise bursts that were 5 mv peak to peak and over as delivered from the pickup.
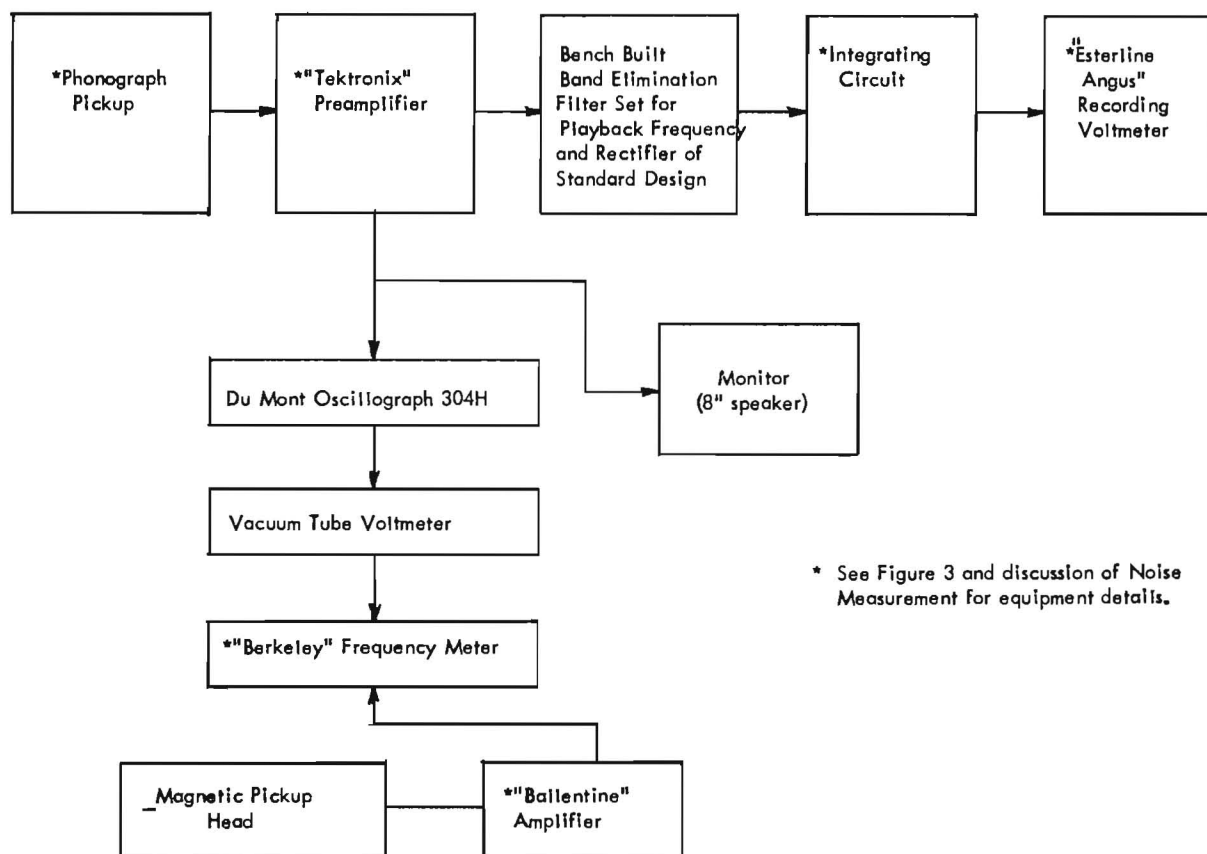
d. *Measurement of Change in Signal.*

An important parameter of disc degradation is change in groove geometry which might result in changes in recorded frequencies, attenuation of recorded signal, and distortion of recorded signal. Possible causes of such groove geometry changes are dimensional changes induced by stress relaxation or chemical degradation. In order to observe and measure possible changes in recorded signal, the standard frequency test disc specimens were used and electronic equipment assembled as shown in Figure 30.

Noise, distortion, and wave form were observed with the oscilloscope and summed on the Esterline Angus recorder. Signal strength and frequency were measured by the VTVM and "Berkeley" frequency meter.

Care was used to prevent surface damage to the discs during testing as the playback qualities of a phonograph record quickly deteriorate when discs are carelessly handled. Disc surfaces were never permitted to slide over other surfaces, as sliding contact with even plastic envelopes can cause scratches from dust particles caught between the surfaces. Rubber gloves were used for disc handling when it was necessary to touch grooved surfaces. Discs were kept clean by using the techniques recommended in Chapter III E. This treatment eliminated the problems of noise caused by dust or electrostatic charges.

The coating failure observed was a cracking, shrinking and delamination of the nitrocellulose film. Changes in noise are reported in db with respect to the original noise level of the disc. Because the first play, after cutting, of acetate discs is much noisier than subsequent plays, the new discs were cleaned, played once, cleaned and played again. The second playback was used as the reference value for noise. Control discs for each test were kept in the conditioning environment at 70° F and 50% R.H. and inspected each time that the test specimens were; no change was observed in the control discs.

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Figure 30. Block diagram of signal measuring equipment.

The blocks in the diagram contain the following text:

*Phonograph Pickup

*"Tektronix" Preamplifier

Bench Built Band Elimination Filter Set for Playback Frequency and Rectifier of Standard Design

*Integrating Circuit

*"Esterline Angus" Recording Voltmeter

Du Mont Oscillograph 304H

Monitor (8" speaker)

Vacuum Tube Voltmeter

*"Berkeley" Frequency Meter

Magnetic Pickup Head

*"Ballentine" Amplifier

*   See Figure 3 and discussion of Noise Measurement for equipment details.

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